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# A CONTRIBUTION TO THE CHEMISTRY OF BUTTER-FAT.[1]

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## II. THE CHEMICAL COMPOSITION OF BUTTER-FAT.

WE have already spoken, in a somewhat general way, of those proximate components into which butter-fat is resolved by the process of saponification. The percentage of glycerol formed by the breaking up of the glycerides and the methods for its estimation were considered in a previous article.[2] We will confine ourselves, therefore, in the present paper to a study of the various fatty acids, both soluble and insoluble, as we obtain them from butter-fat, regarding also, to some extent, the combinations of these different acids with the glycerol base to form what we know as the glycerides, the mixture of which in varying proportions constitutes butter-fat itself.

There is no problem in analytical chemistry more difficult than that of making a quantitative separation of a mixture of different fatty acids. A mixture of two fatty acids is very hard to analyze, much more so a mixture such as we find in butter-fat where at least ten different acids are present. In a case of this kind the most that we can hope for is an approximation, since an exact quantitative separation is impossible in the present condition of analytical chemistry.

[1] Read by title before the New York meeting of the American Chemical Society, December 28, 1898.

[2] This Journal, 21, 612.

Bearing this in mind it need not be thought strange that the analysis of the fatty acids from butter should be a subject upon which scarcely any two writers agree. Chemists are generally quite concordant in determinations of the saponification number and other common constants pertaining to butter-fat analysis; it seems only reasonable, therefore, to attribute such discrepancies as we find in the percentages of the various acids to defective methods of analysis.

In the following table are given the percentages of the different acids in butter-fat according to several authorities:

TABLE V.

| Acid. | 1. Molt.[1] | 2. Koefoed.[2] | 3. Bell.[3] | 4 Blyth.[4] |
|---|---|---|---|---|
| Oleic | 26.52 | 31.11 | 36.1 | 40.40 |
| Stearic | 40.93 | 1.83 | 49.46 | 47.50 |
| Palmitic | 20.00 | 25.62 | | |
| Myristic | | 20.13 | | |
| Lauric | | 7.32 | | |
| Capric | 7.40 | 1.83 | 2.09 | 0.80 |
| Caprylic | | 0.46 | | |
| Caproic | | 1.83 | | 2.40 |
| Butyric | | 1.37 | 6.13 | 3.49 |
| Total | 94.85 | 91.50 | 93.78 | 94.59 |

A difference in the composition of butter-fat itself no doubt explains to some extent the variations in the foregoing table; a difference in composition, however, would hardly warrant such wide discrepancies as we observe between columns 1 and 2 in the case of stearic acid, or between columns 2 and 3 in the case of butyric acid.

A partial separation of the acids of butter into two fractions, one soluble in water and the other insoluble, is very easily effected, as has been shown;[5] the real difficulties of the work may be said to begin only with the final analysis of these two portions.

[1] König: Nahrungs- u. Genussmittel, second edition, p. 281. Original results expressed as glycerides were calculated to fatty acids.

[2] Koefoed: *Bulletin de l'Academie Royale Danoise, 1891*; Abstract in *Analyst*, No. 195, p. 130.

[3] Bell: Analysis and Adulteration of Foods, Vol. II, 48. The fatty acids soluble in water were regarded as butyric acid; the 2.09 per cent. of residual acids were soluble in hot water and had a combining weight of 136.

[4] Blyth: Foods; Their Composition and Analysis, fourth edition, p. 340.

[5] This Journal, 21, 626.

To remove as far as possible the difficulties attending the presence of oleic acid, a butter-fat was selected which gave a rather low iodine absorption; the fat was examined first according to the ordinary methods of analysis and gave the following constants:

| | |
|---|---|
| Saponification number | 232.7 |
| Ether number | 232.5 |
| Iodine number | 29.28 |
| Insoluble acids, per cent | 86.40 |
| Soluble " " | 8.35 |
| Saponification number of insoluble acids | 215.5 |
| Molecular weight " " " | 260.3 |
| Saponification number " soluble " | 572.5 |
| Molecular weight " " " | 98.0 |

One hundred grams of the butter-fat were taken and the soluble and insoluble acids obtained by methods already described. It is an interesting and well-known fact that in the natural fats only acids exist that have an even number of carbon atoms.[1] Besides the acids mentioned in Table V there have been found in butter-fat oxy-acids,[2] and also acetic and arachidic acids;[3] the two latter, however, occur in such minute quantities that their presence is not worth considering.

### ANALYSIS OF THE INSOLUBLE ACIDS.

The two methods most generally followed by chemists for effecting a separation of a mixture of insoluble acids are that of fractional distillation and that of fractional precipitation. In our work the latter method was selected, since it seemed to offer fewer difficulties and fewer sources of error; we have never given the distillation method a fair trial, but a few experiments seemed to indicate that there was an insufficient range in the character of the different fractions and that the whole process was attended with danger of decomposition.[4]

In making the fractional precipitations the method of Heintz[5] was for the most part followed.

The insoluble acids (86.4 grams), obtained from 100 grams of

[1] Richter's Organic Chemistry, Smith's translation of fourth German edition, p. 186.

[2] Bondzynski and Rufi: *Ztschr. anal. Chem.* (1891), 1.

[3] Benedikt: Analyse der Fette, third edition, p. 544.

[4] Koefoed (*Vid. op. cit.* this article, p. 808), however, seems to have used the distillation method with some degree of success.

[5] Heintz: *J. prakt. Chem.*, 66, 1.

butter-fat, were dissolved in ninety-five per cent. alcohol, using such a quantity that nothing crystallized out at 25° C. The solution was then cooled to zero, and after several hours, when crystallization was complete, filtered through a funnel kept cold by means of an ice-jacket. The precipitate of fatty acids, consisting of a white crystalline mass, we will designate as Portion I, and the acids contained in the filtrate as Portion II.

Portion I contained, besides other acids, a small quantity of oleic acid held back mechanically; to remove as much as possible of this, the precipitate of acids was dissolved in a small quantity of hot alcohol, recrystallized in the cold, and filtered as before, the filtrate being added to Portion II.

Portion I was again dissolved in about 500 cc. of hot alcohol, cooled in ice-water, and after recrystallization filtered through the ice-funnel; the precipitate constituted Part 1. The filtrate from Part 1 was evaporated to about 300 cc., cooled in ice-water, and the fat acid crystals filtered off as before; the precipitate constituted Part 2. The filtrate from Part 2 was evaporated to about 150 cc., and the process continued for one more crystallization, Part 3 being obtained; the filtrate from Part 3 was added to Portion II.

The different Parts, 1, 2, and 3, of Portion I were then washed with ether into weighed beakers; after evaporating the ether the acids were dried for a short time at 100°, after which they were cooled, weighed, and preserved for further examination.

Portion II was treated with 100 cc. of a five per cent. solution of magnesium acetate in alcohol, cooled to 0° C., and after crystallization of the magnesium salts was complete, filtered. The precipitate, Part *a*, was washed with 100 cc. of the alcoholic magnesium acetate and the washings added to the original filtrate. The filtrate from Part *a* was then rendered alkaline with ammonia and subjected to a second crystallization at 0° C., when a second precipitate, Part *b*, was obtained; this was filtered off and washed similarly to Part *a*. Nothing more separating from the filtrate at zero, the solution was treated again with ammonia until strongly alkaline; 100 cc. more of the magnesium solution were added and the liquid allowed to stand in the cold for twenty-four hours. The precipitate thus obtained was collected on a

filter and washed with small amounts of the alcoholic magnesium solution ; it constituted Part *c*.

The three fractions of Portion II, Parts *a*, *b*, and *c*, consisting of the magnesium soaps, were then decomposed with dilute hydrochloric acid, and the liberated acids thoroughly washed with hot water to remove all traces of magnesium. The fatty acids from each fraction were then washed with ether into weighed beakers, and, after evaporation of the ether, dried for a short time at 100°, when they were cooled, weighed, and preserved for further examination.

In the analysis of the different fractions from Portions I and II, the saponification number and iodine absorption were determined ; from the former constant the mean molecular weight of the mixture of fatty acids is calculated[1] and from the latter the amount of oleic acid in each fraction is determined :[2] the oleic acid, though sometimes present in but minute quantities, must, nevertheless, be considered in the analysis of the several fractions.

Some uncertainty prevails as to the accuracy of calculating the percentage of oleic acid in a mixture of glycerides or fatty acids from the iodine number alone. There is not only the possibility of other unsaturated acids existing besides oleic acid, but also the danger that iodine may be substituted as well as added in the course of the reaction. These objections are no doubt valid in the case of many vegetable and fish oils, but apply with less force to the common fats of animal origin, which contain, so far as known, only one unsaturated acid ; *viz.*, oleic.

The possibility of iodine being substituted, with the glycerides or acids of butter-fat at least, appears to us to be very slight ; after removing the olein or oleic acid by repeated crystallizations of the fat or fatty acids, the percentage of iodine absorbed can be reduced practically to nothing, thus showing that with the higher saturated glycerides and acids but very little, if any, substitution occurs.

We have selected as the first step in the calculations the de-

[1] By the formula $M = \frac{56100}{S}$. Benedikt: Analyse der Fette, third edition, p. 163.

[2] By the formula $O = \frac{100}{90.07} I = 1.1102 I$, 90.07 being the theoretical iodine absorption of pure oleic acid. Benedikt : *Ibid.*, p. 173.

termination of the mean molecular weight of the fatty acids in each fraction after deducting the oleic. This result is obtained by the following formula :

$$\frac{100}{m} - \frac{O}{282} = \frac{100-O)}{x};$$

or

$$x = \frac{282\ m\ (100-O}{28200-mO}.$$

$O$ = percentage of oleic acid as calculated from iodine number.
$m$ = mean molecular weight of original acids.
$x$ = " " " after deducting oleic.

If now we assume that there are not more than two acids present in each fraction besides the oleic and that these acids are adjacent homologues of even carbon atoms, then the relative percentage of each acid can be determined from the following formulas :

$$x + y = 100;$$

$$\frac{x}{m_1} + \frac{y}{m_2} = \frac{100}{m};$$

from which

$$x = \frac{100\ m_1\ (m-m_2)}{m\ (m_1-m_2)};$$

$$y = \frac{100\ m_2\ (m_1-m)}{m\ (m_1-m_2)}.$$

$m$ = mean molecular weight of the two acids.
$m_1$ and $x$ = molecular weight and percentage, respectively, of the higher acid.
$m_2$ and $y$ = molecular weight and percentage, respectively, of the lower acid.

The expression $m_1-m_2$ for the saturated fatty acids of even carbon atoms equals 28; substituting this value in the previous equations :

$$x = \frac{100\ m_1\ (m-m_2)}{28\ m};$$

$$y = \frac{100\, m_2\, (m_1 - m)}{28\, m}.$$

To ascertain what acids are present in any particular fraction, it is only necessary to observe between what two homologues the mean molecular weight of the fraction falls, after deducting the oleic.

The formulas, as derived from the two preceding general equations, for calculating the percentage of stearic acid ($S$) and palmitic acid ($P$) in a mixture of the two, knowing the mean molecular weight ($m$), are as follows:

$$S = \frac{28400\ (m - 256)}{28\, m};$$

$$P = \frac{25600\ (284 - m)}{28\, m}.$$

In the same way for palmitic acid ($P$) and myristic acid ($M$):

$$P = \frac{25600\ (m - 228)}{28\, m};$$

$$M = \frac{22800\ (256 - m)}{28\, m}.$$

The analytical data of the various fractions belonging to Portions I and II, together with the calculated amounts of the different acids, are given in the following table:

[1] There is some difference among chemists as to the proper formula to use for calculating the percentage of two acids from the mean molecular weight. Benedikt, Hehner, and the majority of German chemists take the formula $\frac{x}{m_1} + \frac{y}{m_2} = \frac{100}{m}$, while the calculations of Allen, Prescott, and many others are based upon the formula $xm_1 + ym_2 = 100\, m$. The former formula seems to us the only correct one. To take for example a simple case:

| | Per cent. |
|---|---|
| 1 molecule stearic acid weighs 284 | = 52.59 |
| 1 " palmitic " " 256 | = 47.41 |
| 2 molecules of mixture weighs 540 | = 100.00 |

Mean molecular weight of mixture $= \frac{540}{2}$ or 270.

If we determine now from the two formulas, what percentages of stearic and palmitic acids will give a mean molecular weight of 270, we obtain 52.59 per cent. stearic and 47.41 per cent. palmitic, the theoretical results, by the formula $\frac{x}{m_1} + \frac{y}{m_2} = \frac{100}{m}$; whereas the formula $xm_1 + ym_2 = 100\, m$ gives exactly fifty per cent. of each.

TABLE VI.

| | Portion I. | | | Portion II. | | | Total per cent. |
|---|---|---|---|---|---|---|---|
| | Part 1. | Part 2. | Part 3. | Part *a*. | Part *b*. | Part *c*. | |
| Weight of fraction | 5.20 grams | 6.01 grams | 21.13 grams | 9.22 grams | 7.82 grams | 5.05 grams | .... |
| Mean molecular weight of fraction | 272.2 | 260.0 | 260.7 | 254.6 | 254.5 | 251.2 | .... |
| Iodine number of fraction | 3.44 | 10.94 | 15.03 | 8.41 | 19.85 | 25.12 | .... |
| Per cent. oleic acid in fraction | 3.82 | 12.14 | 16.68 | 9.34 | 22.03 | 27.88 | .... |
| Mean molec'lar weight after deducting oleic | 271.8 | 257.2 | 256.8 | 252.1 | 247.7 | 241.0 | .... |
| Weight of stearic acid | 2.95[1] grams | 0.25 gram | 0.56 gram | .... | .... | .... | 3.76 |
| " " palmitic " | 2.05 grams | 5.03 grams | 17.05 grams | 7.32 grams | 4.44 grams | 1.79 grams | 37.68 |
| " " myristic " | .... | .... | .... | 1.05 grams | 1.66 grams | 1.85 grams | 4.56 |
| Undetermined | | | | | | | 7.90[2] |

[1] Contains also the oxy-acids, a correction for which will be introduced later.

[2] Found by subtracting the sum of the acids determined and the oleic acid 32.50 per cent (calculated from iodine absorption) from 86.40, the total per cent. of insoluble acids.

The 7.90 per cent. of undetermined acids, which escaped precipitation, includes all of the lauric acid and no doubt a considerable part of the myristic; the percentage of each of these acids can be arrived at in another way. Having five members present in a mixture of fatty acids and knowing the molecular weight and percentage of three of them, the mean molecular weight of the other two can be determined by the following formula:

$$\frac{a}{m_1} + \frac{b}{m_2} + \frac{c}{m_3} + \frac{100-(a+b+c)}{x} = \frac{100}{m}.$$

$a$, $b$, and $c$ are the percentages of the three known acids and $m_1$, $m_2$, and $m_3$ their respective molecular weights. $m$ is the mean molecular weight of the whole mixture and $x$ the mean molecular weight of the two acids sought.

Applying this formula to the case in hand we have for the three known acids, oleic, stearic, and palmitic, the following percentages:

TABLE VII.

| | In 100 parts of butter-fat. | In 100 parts of acids. |
|---|---|---|
| Oleic acid (from iodine number) ..... | 32.50 | 37.61 |
| Stearic acid ..... | 3.76 | 4.35 |
| Palmitic acid ..... | 37.68 | 43.61 |
| Myristic and lauric acids ..... | 12.46 | 14.43 |
| Total ..... | 86.40 | 100.00 |

The mean molecular weight of the insoluble fatty acids from the butter was 260.3; substituting these values in the formula we obtain the following equation:

$$\frac{37.61}{282} + \frac{4.35}{284} + \frac{43.61}{256} + \frac{14.43}{x} = \frac{100}{260.3};^{1}$$

or $$0.13339 + 0.01532 + 0.17035 + \frac{14.43}{x} = 0.38418;$$

or $$\frac{14.43}{x} = 0.06512;$$

whence $$x = 221.6.$$

This figure for the mean molecular weight falling between 200

[1] Strictly the formula should also take into account the oxy-acids; this, however, would make no difference with the final results, inasmuch as the mean molecular weight of the determined acids (and hence of the undetermined) would remain the same in either case.

and 228 would indicate a mixture of lauric and myristic acids. Knowing the mean molecular weight ($m$) of a mixture of myristic ($M$) and lauric ($L$) acids, the percentages of each may be calculated from the formulas

$$M = \frac{22800(m-200)}{28\,m},$$

$$L = \frac{20000(228-m)}{28\,m}.$$

Substituting the value 221.6 for $m$ in the preceding equations we obtain 79.37 per cent. myristic and 20.63 per cent. lauric acid; this would give in the 12.46 parts of undetermined acids 9.89 parts of myristic and 2.57 parts of lauric acid for 100 parts of butter-fat.

Such a method for analyzing a mixture of fatty acids as the one described manifestly presents many crudities; the method of Heintz, however, "supplies the only means of obtaining an insight into a mixture of non-volatile acids."[1] Unfortunately, "there is no practical method of proving that two and only two acids are present"[1] in any particular fraction, and therein lies the principal fault of the method. Allen observes that "as a rule if the mixed fatty acids be divided into a sufficient number of fractions, each fraction will contain only two homologues,"[2] and this assumption seems to be a fairly reasonable one.

The oleic acid is a disturbing factor throughout the whole process and its presence must be taken into account in the analysis of the different fractions. We believe too little attention has been paid to this point. The method could be improved greatly if there were some good means of removing the oleic acid at the beginning of the process. The plan of converting the mixture of acids into the lead soaps and removing the lead oleate with ether would not work well on a large quantity of acids, and besides this the process does not effect a perfect separation.

We have taken no account thus far of the oxy-fat acids: that such acids are present in butter-fat seems certain from the acetyl figure which the insoluble acids always give. The oxy-acids probably do not exist in the fat as it is secreted from the lacteal

[1] Hehner and Mitchell: *Analyst*, No. 249, p. 317.
[2] Commercial Organic Analysis, third edition, Vol. II, Part 1, p. 242.

glands, but are later oxidation products of the oleic acid—dioxystearic[1] acid being no doubt principally formed.

$$\underset{\text{Oleic acid.}}{C_{18}H_{34}O_2} + O + H_2O = \underset{\text{Dioxystearic acid.}}{C_{18}H_{34}O_2(OH)_2}.$$

Owing to the low solubility of the higher oxy-acids in cold alcohol, any oxy-acids present would come down with the first crystallization (Part I, Table VI), and this fact would alter somewhat the percentages of the acids in this fraction.

Benedikt has devised a formula by means of which the percentage of an oxy-acid in a mixture of fatty acids can be calculated from the acetyl number, provided that the constitution and molecular weight of the oxy-acid is known. The equation is

$$x = \frac{100\,c\,m}{a(56100-42c)},^{2}$$

in which $c$ = the acetyl number.

$a$ = the number of hydrogen atoms in the oxy-acid replaceable by acetyl.

$x$ = percentage sought of the oxy-acid having a molecular weight $m$.

Applying this formula to the insoluble acids from the average butter-fat having an acetyl number of 4.1 we would obtain for dioxystearic[3] acid 1.16 per cent., or calculated to the original butter-fat 1.00 per cent. of oxy-acid.

There are no doubt other oxy-acids present besides the dioxystearic in the mixture of insoluble acids, so that the results from this method of calculation can only be considered approximate. The percentage of oxy-acids in butter-fat increases with time and is therefore never a fixed quantity. The gradual increase in the acetyl number, together with the decrease in the saponification number of the insoluble acids, with the age of a butter-fat, goes to show that oxy-acids of a high molecular weight are continually being formed. This fact will be explained more fully under the subject of "Rancidity in Butter-fat."

If we introduce a correction for the percentage of oxy-acid, as found, in the first fraction of the insoluble acids and recalculate

[1] A Scala (Staz. sperim. agr. ital. (1897), p. 613, shows that this acid is formed among the oxidation products of oleic acid.

[2] Benedikt: *Monatsh. Chem.* (1890), 95, and Analyse der Fette, third edition, p. 178.

[3] For dioxystearic acid in the formula $a = 2$ and $m = 316$.

the stearic and palmitic acids, the analysis of Part I would then be :

| | Grams. |
|---|---|
| Dioxystearic acid | 1.00 |
| Stearic acid | 1.02 |
| Palmitic acid | 2.98 |

The complete analysis of the insoluble acids from 100 parts of butter-fat accordingly would be :

| | Grams. |
|---|---|
| Dioxystearic acid | 1.00 |
| Oleic acid | 32.50 |
| Stearic acid | 1.83 |
| Palmitic acid | 38.61 |
| Myristic acid | 9.89 |
| Lauric acid | 2.57 |
| Total | 86.40 |

A noteworthy fact in connection with the above results is the low percentage of stearic acid in butter-fat. This is somewhat contradictory to the statements which we find given by many authorities on the subject who regard stearic as one of the principal acids in butter-fat, it being placed, by some writers, as high even as forty per cent. We believe that these statements should be modified somewhat; when we consider that oleic acid of molecular weight 282 constitutes over one-third of the insoluble acids from butter-fat, it is self-evident that the percentage of stearic acid of molecular weight 284 must be small in comparison with that of its lower homologues, to give a mean molecular weight of 261 to the whole mixture.

Koefoed,[1] in his analysis of butter-fat, obtained only 1.83 per cent. stearic acid which, by a strange coincidence, is exactly the same quantity found by us after correcting for the oxy-acids.

Hehner[2] and Mitchell, by removing the oleic and lower insoluble acids with dilute alcohol and analyzing the residue, obtained only from one and three-tenths to three and six-tenths per cent. stearic acid; the same authorities, with their process[3] of removing all other acids by treatment of the insoluble acids at 0° C. with a saturated solution of stearic acid in alcohol,

[1] *Vid. op. cit.*, p. 803 of this article.
[2] *Analyst*, No. 249, p. 321.
[3] *Ibid*, p. 322.

obtained in over 100 determinations only minute quantities of stearic acid and in many cases none at all.

This low percentage of stearic acid should rank with the high percentage of soluble fatty acids, as one of the characteristic differences between butter and other animal fats.

### ANALYSIS OF THE SOLUBLE ACIDS.

A great many methods have been devised for the analysis of a mixture of the lower soluble fatty acids, but very few of them seem practicable in actual work. The method of fractional distillation, which suggests itself perhaps first of all, does not give good results when working with a small quantity of acids, the principal difficulty which we have found being that of not securing a wide enough range in the character of the several fractions.

No more satisfactory were the methods based upon the difference in the chemical affinities of the various acids.[1] A neutralized solution of the mixed soluble acids was decomposed with successive portions of tenth-normal sulphuric acid, the liquid being subjected to distillation after each addition of acid. The various distillates were neutralized with tenth-normal barium hydroxide and the mean molecular weights of the acids in each fraction determined. A difference was found in the acids of the several successive distillates, but not a distinctive one, the several molecular weights varying only from two to three units. The theory of the method is borne out, but imperfectly. In one experiment the mean molecular weight of the acids in the first fraction was 102.7; the succeeding fractions gave in their order 99.4, 96.8, 94.8, 93.9, 91.2, and 88.7. It is seen that the mean molecular weights of the acids in the successive distillates decrease until we have practically pure butyric acid in the final fraction; the differences are too small, however, to form any basis for calculations.

The method of Duclaux,[2] based upon the difference in ratio of vaporization of the various acids from their solution, did not appear adaptable to the present instance where more than two acids were present.

The following method, worked out by the writer, was found

1 Allen: Commercial Organic Analysis, third edition, Vol. I, p. 487.

2 Duclaux: *Ann. Chem. Phys.* [5], 11, 233.

to give a considerable range in the character of the different fractions, with but little trouble of execution; it is based upon the difference in the solubility[1] of the various lower homologues in water at different temperatures.

One gram of the mixed acids is weighed out into a small fifty cc. flask and treated with twenty-five cc. of distilled water, previously cooled to nearly 0° C. The flask is placed in a beaker of ice and agitated frequently for about five minutes; the contents of the flask are then poured into a small filter placed in a funnel surrounded by ice, and the flask rinsed out with small portions (five cc.) of the cold water, the rinsings being poured upon the filter and allowed to run into the beaker holding the original filtrate. Not more than twenty-five cc. of water are used for the washing. The acids left on the filter are washed back into the flask with about twenty-five cc. of distilled water at 30° and, after being kept at this temperature for five minutes with frequent shaking, again filtered. The flask is rinsed out and the acids on the filter washed as before with small quantities of water (about twenty-five cc. in all) at 30°, the combined filtrate and washings constituting Fraction 2. The acids remaining on the filter are then treated successively in the same manner with water at 60° and 95°, Fractions 3 and 4 being thus obtained.[2]

The various fractions are next titrated with standard tenth-normal barium hydroxide, using phenolphthalein as indicator; the solutions of the barium salts are evaporated to dryness in weighed platinum dishes, and the residues dried to constant weight at 100°. From the weight of the residue and the weight of barium oxide contained therein, the mean molecular weight of the acids in each fraction is determined.[3] The amount of barium oxide in the residue can be calculated either from the volume of solution used to neutralize the acids, or by igniting

[1] Storer (Dictionary of Chemical Solubilities) gives the following:
Butyric acid soluble in water in all proportions:
Caproic acid soluble in 96 parts of water at 7° C.
Caprylic " " " 400 " " " " 100° C.
Capric " " " 1000 " " " " 20° C.

[2] The physical characters of the acids are observed to change during the process of washing. After the removal of the first fraction the acids lose their mobility and acquire a thick, oily consistency. The strong rancid smell, characteristic of butyric acid, entirely disappears with the removal of the second fraction, while the residual acids possess a very peculiar odor, resembling somewhat that of perspiration.

[3] This Journal, 21, 628.

the residue with sulphuric acid and weighing the barium sulphate.

In one experiment, conducted by the method just described, there were found for the different fractions the following results:

TABLE VIII.

| | Temperature of water used for washing. | Mean molecular weight of acids. |
|---|---|---|
| Fraction No. 1..... | 5° C. | 91.4 |
| " " 2..... | 30° C. | 113.1 |
| " " 3..... | 60° C. | 123.6 |
| " " 4..... | 95° C. | .... |

The quantity of acids left after treating with water at 60° amounted to only a few milligrams and so was insufficient for an accurate molecular weight determination.

The weight of acids in each fraction can be found from the formula

$$W = \frac{M\,n}{10{,}000},$$

in which $W$ equals the weight in grams of acids, $M$ the mean molecular weight of the acids, and $n$ the number of cubic centimeters of tenth-normal alkali used for their neutralization.

If we assume that only two acids are present in each fraction, an assumption[1] probably not very far from true, the percentage of each acid can be calculated from the mean molecular weight according to the general formulas already given. For a mixture of butyric ($B$) and caproic ($C$) acids,

$$B = \frac{8800\ (116-m)}{28\ m};$$

$$C = \frac{11600\ (m-88)}{28\ m}.$$

For a mixture of caproic ($C$) and caprylic ($C_1$) acids,

$$C = \frac{11600\ (144-m)}{28\ m};$$

$$C_1 = \frac{14400\ (m-116)}{28\ m}.$$

[1] The wide difference in the solubility of the lower acids in water would almost preclude the possibility of finding more than two acids in each fraction. There is, however, this possibility, which experiments would seem to indicate, that the solubility of the higher acids in water is somewhat greater if lower acids are present. This is a point well worth investigation.

Several analyses of the soluble acids from butter-fat conducted by the method described gave the following average composition :

| | Per cent. |
|---|---|
| Butyric acid | 65.28 |
| Caproic " | 25.00 |
| Undetermined | 9.72 |

The mean molecular weight of the undetermined acids can be calculated from the equation,

$$\frac{65.28}{88} + \frac{25.00}{116} + \frac{9.72}{x} = \frac{100}{98},$$

from which $x = 154$. This value, falling between 144 and 172, would indicate that the undetermined acids consisted of caprylic and capric. From the mean molecular weight ($m$) the percentages of caprylic ($C_1$) and capric ($C_2$) acids can be calculated as follows :

$$C_1 = \frac{14400\ (172-m)}{28\ m};$$

$$C_2 = \frac{17200\ (m-144)}{28\ m}.$$

In the undetermined residue of 9.72 per cent. we find from the above formulas sixty parts of caprylic and forty parts of capric acid, or 5.83 per cent. caprylic and 3.89 per cent. capric in the total mixture of soluble acids.

Calculating the analysis to the 8.35 per cent. of soluble acids in the original butter-fat we obtain :

| | Per cent.[1] |
|---|---|
| Butyric acid | 5.45 |
| Caproic " | 2.09 |
| Caprylic " | 0.49 |
| Capric " | 0.32 |
| Total | 8.35 |

[1] In connection with these percentages for the soluble acids it will be of interest to quote the results of two French chemists :

Duclaux (*Compt. rend.*, 102, 1022) found in eight samples of butter examined 3.38 to 3.60 per cent. butyric and 2.08 to 2.26 per cent. caproic acid. Violette (*Compt. rend.*, 111, 345) found for good butter 5.32 to 6.06 per cent. butyric and 3.22 to 3.66 per cent. caproic acid. Apparently no attempts were made by either of these chemists to determine the caprylic and capric acids.

For other results see Table V.

## SUMMARY.

The results of the analysis of the mixed acids from the butter-fat examined, together with the equivalent percentages of triglycerides, are given in the following table:

TABLE IX.

| Acid. | Percentage of acid. | Percentage of triglycerides. |
|---|---|---|
| Dioxystearic | 1.00 | 1.04 |
| Oleic | 32.50 | 33.95 |
| Stearic | 1.83 | 1.91 |
| Palmitic | 38.61 | 40.51 |
| Myristic | 9.89 | 10.44 |
| Lauric | 2.57 | 2.73 |
| Capric | 0.32 | 0.34 |
| Caprylic | 0.49 | 0.53 |
| Caproic | 2.09 | 2.32 |
| Butyric | 5.45 | 6.23 |
| Total | 94.75 | 100.00 |

Other bodies, such as coloring-matter, lecithin, cholesterin, phytosterin, etc., which occur in butter-fat in only minute quantities, have not been considered in the above analysis. These substances go to make up the unsaponifiable matter of butter-fat, the total amount of which we have found to be only about one-tenth per cent.

We have made an elementary analysis of butter-fat and find the agreement between the actual percentages of carbon, hydrogen, and oxygen, and the theoretical figures as calculated from the percentages of the various glycerides in the preceding table, to be very close.

| | Carbon. | Hydrogen. | Oxygen. |
|---|---|---|---|
| Actual | 75.17 | 11.72 | 13.11 |
| Theoretical | 74.86 | 11.71 | 13.43 |

The close agreement between these two sets of results would indicate that the figures expressing the percentages of acids and glycerides in Table IX are not very far removed from the truth.

## THE GLYCERIDES OF BUTTER-FAT.

Experiments of Bell,[1] Blyth,[2] and other chemists indicate that there are certain glycerides in butter-fat of a complex nature;

[1] Allen: Commercial Organic Analysis, third edition, Vol. II, Part 1, p. 180.
[2] Blyth: Foods; Their Composition and Analysis, fourth edition, p. 340.

that instead of simply one acid we may have two or even three different acid radicals in the same molecule.

If a mixture of tributyrin, tripalmitin, and triolein be prepared and treated with alcohol, it is possible to extract the tributyrin completely. With butter-fat, on the other hand, such an extraction cannot be made, a fact due without doubt to the butyric acid being combined with certain higher fat acids to the same glycerol radical.[1] In confirmation of this, Blyth and Robertson[2] have isolated from butter-fat a crystalline glyceride of the formula

$$C_3H_5(C_4H_7O_2)(C_{16}H_{31}O_2)(C_{18}H_{33}O_2),$$

a mixed ester of butyric, palmitic, and oleic acids.

While a part of the butyric, palmitic, and oleic acids in butter-fat is no doubt bound up together in one molecule, it is also certain that these acids exist in glycerides of a different nature. Experiments seem to indicate that there are present glycerides which contain at least two radicals of one acid in the same molecule and probably three. Tripalmitin certainly exists and has been isolated by us in a state of comparative purity. The separation of all the various glycerides is a problem at present beyond the power of the chemist. It is only possible to make a few rough separations and from certain analytical data draw some general conclusions.

If a melted butter-fat is allowed to stand for some time at about 25° C., a crystalline deposit will separate out. By filtering we obtain two portions,—a clear transparent oil, the so-called butter-oil, and a solid mass comprising all the glycerides of higher melting-point. If the butter-oil is cooled another deposit will form; by repeating the process of filtering and cooling, the congealing-point of the oil can be reduced from 25° C. to below 10° C. These different fractions of oil will be found to differ in chemical as well as physical properties, as can be seen from the following table:

TABLE X.

| Congealing-point. | Iodine number. | Saponification number. |
|---|---|---|
| 25° C. | 35.05 | 233.0 |
| 12° C. | 39.24 | 234.0 |
| 9° C. | 40.95 | 235.6 |

[1] Benedikt: Analyse der Fette, third edition, p. 544.

[2] *J. Lond. Chem. Soc.*, Proceedings (1889), 5

The increase in the iodine and saponification numbers, as the congealing-point decreases, is due to an increase in the percentages of oleic and the soluble acids. The quantity of soluble acids increases much faster than the saponification number indicates, since the increase in oleic acid tends to keep this constant down.

The butter-oil of 9° congealing-point contains, according to its iodine absorption, over forty-five per cent. oleic acid, which quantity is considerably in excess of the percentage required by such a glyceride as that of Blyth and Robertson. Indications would point to the presence of glycerides containing at least two radicals of oleic acid in the molecule, and there is no reason to doubt the existence of triolein itself.

The solid mass left on the filter, after removing the butter-oil, still contains a high percentage of oleic acid; it resembles butter-fat itself in outward appearance. The body is somewhat harder, however, than butter-fat, possessing also a higher melting-point and lower content of soluble acids. For want of a better name, we have termed this residue, left after removing the oil, *butter-palmitin*. The relation between the constants of butter-oil, butter-palmitin, and the original butter-fat can be seen from the following table:

TABLE XI.

| | Melting-point. | Saponification number. | Iodine number. | Reichert number. |
|---|---|---|---|---|
| Original butter-fat | 33° | 231 | 31.00 | 15.30 |
| Butter-oil | 25°[1] | 233 | 35.05 | 18.18 |
| Butter-palmitin | 38° | 228 | 27.66 | 11.23 |

By subjecting the butter-palmitin to repeated crystallizations from some suitable solvent (chloroform was found to be the best), it is possible to remove practically all of the oleins and lower glycerides and to obtain almost pure tripalmitin itself. The body possesses a beautiful, white, flaky appearance, crumbles readily between the fingers, and leaves no oily spots when spread on paper. Traces of oleic, stearic, and lower soluble acids are generally present as impurities. A specimen of the glyceride gave a saponification number of 207; the saponification number of tripalmitin, according to theory, is 208.

[1] Congealing-point.

If we treat butter-fat with hot ninety-five per cent. alcohol, then cool, filter, and evaporate the alcohol, a small quantity of a gum-like fat is left. A body so obtained melted at 22.5° C., gave a saponification number of 257, an iodine number of 26.15, and yielded about seventy-nine per cent. insoluble and fourteen per cent. soluble acids. The small percentage of the body obtained and its high saponification number (higher than that required for an oleopalmitobutyrin), would point to glycerides containing more than one radical of the lower acids.

In conclusion, the most that we can say is that, while the evidence is strongly in favor of the existence of complex glycerides, there are equally good reasons for believing in the existence of simpler bodies. An analysis of the fatty acids from the different fractions of the butter-oil and butter-palmitin would throw much light upon the constitution of the glycerides contained therein; for such work, however, our time has been too limited. We hope, if possible, in the future to continue our work in this direction.

NOTE.

Inasmuch as the reliability of the analyses, contained in the foregoing paper, is dependent to a great extent upon the accuracy of certain chemical methods, a word should be said in regard to the extent of error which is involved in work of the latter kind.

Nearly all of the calculations concerning molecular weights and percentages were based upon the determination of two constants, the saponification number and iodine absorption. Wherever possible, duplicate, and in some cases triplicate, determinations of these constants were made. The difference between two determinations of the saponification number rarely exceeded $\pm 1$, and the error between duplicate determinations of the iodine absorption was seldom greater than $\pm 0.1$; these differences would affect only slightly the calculation of the mean molecular weights and percentages.

In standardizing the different solutions used for the volumetric work we have employed a few methods, which for speed and accuracy we think superior to some other processes in more general use; we will therefore mention them briefly in this connection.

Tenth-normal barium hydroxide is standardized by evaporating a measured quantity (twenty to fifty cc.) in a weighed platinum dish with a slight excess of dilute sulphuric acid, igniting the residue, and weighing the barium sulphate.

Tenth-normal sulphuric acid is standardized in a similar way. Twenty cc. of the acid are measured from a burette into a weighed platinum dish and the solution carefully neutralized with tenth-normal barium hydroxide, using phenolphthalein as indicator; the liquid is evaporated to dryness, the residue ignited, and the weight of barium sulphate determined. The weight of barium sulphate found divided by 0.2335 will give the factor for the tenth-normal sulphuric acid. In this way the barium hydroxide and sulphuric acid can both be standardized by a single operation. Determinations can be made in one-fourth less time by this process than by the usual method of precipitation and with no difference as regards accuracy of results. The barium hydroxide used should be perfectly pure and free from other alkali; if not C. P. it can be easily purified by recrystallization.

The two tenth-normal solutions just mentioned can be used for standardizing the half-normal alcoholic potash and half-normal hydrochloric acid employed for determining saponification numbers. Another method, which we have been accustomed to apply as a check, has proved very successful in the case of standardizing these last-named solutions.

Ten cc. of the half-normal potash solution are carefully neutralized with the half-normal hydrochloric acid, using phenolphthalein, and the number of cubic centimeters used carefully noted; the liquid, after evaporating off the alcohol, is diluted to about fifty cc. and an excess of platinic chloride solution added. The potassium platinichloride is precipitated and determined in the usual way, a Gooch crucible being used for collecting the precipitate. The weight of potassium platinichloride divided by 1.2145 will give the factor for the half-normal alcoholic potash solution; from the number of cubic centimeters of the acid used to neutralize the potash the factor for the half-normal hydrochloric acid is found. Factors obtained for the half-normal solution by precipitation with platinic chloride and by titration against the tenth-normal solutions have always showed a very close agreement.

# HALIDES AND PERHALIDES OF THE PICOLINES.

By Paul Murrill.[1]

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THE history of the periodides has been given in papers previously published from this laboratory,[2] and work upon various phases of the problem has been in progress here since 1895.[3] For our present knowledge of picoline we are chiefly indebted to the labors of Anderson,[4] Baeyer,[5] Dewar,[6] and Ramsay.[7] This research was undertaken as an extension of the work of Prescott and Trowbridge on pyridine and quinoline, and for the purpose of studying the homologues in the series, inasmuch as the presence of a side-chain can be considered as being a step nearer to the composition of the vegetable alkaloid.

## EXPERIMENTAL PART.

### I. NORMAL IODIDES.

*α-Picoline Methyl Iodide*, $C_5H_4(CH_3)N.CH_3I$.—This compound was prepared and described by Ramsay[8] in 1876, and the same method of preparation was used. Picoline and methyl iodide unite readily at ordinary temperatures with evolution of heat, so that a reflux condenser is necessary to prevent loss of methyl iodide. The product soon solidifies to a yellowish mass, and is recrystallized from absolute alcohol, from which solvent it comes out in long white needles, melting at 224° (Ramsay 227°).

| | Calculated for $C_6H_7N.CH_3I$. | Found. |
|---|---|---|
| Iodine | 53.97 | 53.5[9] |

The isomeric β- and γ-compounds were not obtained pure but

[1] A thesis presented to the council of the graduate school of the University of Michigan, for the Degree of Doctor of Philosophy, June, 1899.

[2] A. B. Prescott: The Periodides, this Journal, **17**, 775 (1895); Periodides of the Alkaloids, *Pharm. Review*, **14**, 172 (1896).

[3] Prescott and Trowbridge: Periodides of Pyridine, this Journal, **17**, 859, and **19**, 322; Trowbridge and Diehl: Halides and Perhalides of Pyridine, this Journal, **19**, 558; Trowbridge: Perhalides of Quinoline, this Journal, **21**, 66; Gomberg: Perhalides of Caffeine, this Journal, **18**, 347; Prescott and Gordin, Alkaloidal Periodides, this Journal, **20**, 706.

[4] *Ann. Chem.* (Liebig), **60**, 86 (1846); **70**, 32 (1849); **80**, 44 (1851); **94**, 358 (1855); *Edinb. Phil. J.*, 146 and 291 (1846); *Phil. Mag.*, (3), **33**, 174 and (4), **9**, 291.

[5] *Ber. d. chem. Ges.*, **2**, 398 (1869).

[6] *Chem. News*, **23**, 38 (1871)

[7] *Phil. Mag.*, (5) **2**, 269 (1876); **4**, 241 (1877); **6**, 19 (1878); *Ber. d. chem. Ges.*, **11**, 1836.

[8] *Phil. Mag.*, (5), **2**, 277.

[9] For methods of analysis see last part of this paper.

the results show that their melting-points are in all probability considerably lower than that of the $\alpha$-compound. Five grams of picoline boiling at 137°–140° (the last fraction of a 400 grams lot) were converted into the methiodide and crystallized once from absolute alcohol. These crystals appeared to be a mixture of two or more kinds, and melted at 183°. It was further converted into the triiodide described further on, and in view of later facts appears to have been a mixture of the $\alpha$- and $\gamma$-compounds. A mixture of the $\alpha$- and $\beta$-compounds was obtained as an oil, and this was also used in the preparation of periodides.

*$\alpha$-Picoline Ethyl Iodide*, $C_6H_7N.C_2H_5I$.—This compound was prepared by Anderson[1] in 1855, and by him the melting-point is said to be below 100°, but is not definitely stated. He prepared it by heating picoline and ethyl iodide in a sealed tube, but this has been found to be unnecessary, and instead the constituents were heated on a water-bath under reflux condenser. The reaction is complete in two hours, and on cooling the oil solidifies to a yellowish mass. The excess of ethyl iodide is distilled off, and the residue dissolved in hot absolute alcohol. When cooled slightly, ether is added as long as the precipitate redissolves on shaking, and then it is allowed to crystallize. From this it comes out in large feathery plates, colorless or faintly yellow. It melts at 123°, and contains 50.8 per cent. iodine; theory 50.93 per cent.

*Picoline Propyl Iodide*, $C_6H_7N.C_3H_7I$.—Prepared by heating the constituents on the water-bath under reflux condenser. The action is complete in about two hours, and a thick sirup is formed, which solidifies to a crystalline mass on cooling. A portion was dried on porous plates in a desiccator, and the remainder crystallized from a very small amount of hot absolute alcohol. Yellowish needles formed, melting at 77°.

| | Calculated for $C_6H_7N.C_3H_7I$. | Found. Crude. | Found. Crystallized. |
|---|---|---|---|
| Iodine | 48.23 | 45.2 | 48.3 |

*Picoline Isopropyl Iodide*, $C_6H_7N.C_3H_7I$.—Prepared in same manner as preceding, using instead isopropyl iodide. Needles which melt at 142°, and contain 48.4 per cent. iodine.

*Picoline Butyl Iodide*, $C_6H_7N.C_4H_9I$.–Preparation same as the pre-

[1] *Phil. Mag.*, (4), 9, 214; *Ann. Chem.* (Liebig), 94, 361.

ceding. The residue was crystallized once from a very small amount of absolute alcohol, washed with ether and dried on a porous plate in a vacuum desiccator. These were straw-colored crystals, melting at 98°.

| | Calculated. | Found. |
|---|---|---|
| Iodine | 45.79 | 45.8 |

*Picoline Isobutyl Iodide*, $C_6H_7N.C_4H_9I$.—A light yellow sirup, not solidifying at —15°. Prepared by allowing a mixture of the constituents to stand at room temperature for two weeks, also by heating the same mixture for six hours at 100°. If either the mixture or the addition-product is heated much above 100°, decomposition takes place, and on cooling crystals of picoline hydriodide appear. It is very hygroscopic, and no analysis of this compound was made, but these products were used in the preparation of the periodides described later.

*Picoline Secondary Butyl Iodide*, $C_6H_7N.C_4H_9I$.—This compound was prepared inthe same manner as the preceding, but it is much more unstable, and it is doubtful if it was obtained entirely free from hydriodide. When heated, or even if kept on a porous plate in a desiccator, it gradually disappears, breaking up into picoline, hydriodic acid, and (probably) pseudo-butylene. When prepared by allowing the constituents to stand two weeks at room temperature it is a light yellow sirup, which becomes crystalline on cooling to 0°. When prepared by heating the constituents for six hours at 100°, it is obtained as a straw-colored crystalline solid, which could not be dried sufficiently to obtain a melting-point. Both preparations were converted into periodides described later.

| | Calculated. | Found. |
|---|---|---|
| Iodine | 45.79 | 44.64 |

*Picoline and Tertiary Butyl Iodide*.—Picoline reacts with tertiary butyl iodide at 100° in the same way that pyridine[1] does; *i. e.*, with formation of the hydriodide, and liberation of isobutylene. The resulting compound melted at 98°, and seemed to be a mixture, so that perhaps a little of the butyl iodide was formed. Analysis showed 51.76 per cent. of iodine.

Picoline and tertiary butyl chloride do not react at the boiling-point of the mixture.

[1] Lippert: *Ann. Chem.* (Liebig), 276, 184.

*Picoline Isoamyl Iodide*, $C_7H_7N.C_5H_{11}I$.—Amyl iodide (boiling at 148°) was heated with picoline on a sand-bath under reflux condenser. When cold the residue was dissolved in a very small quantity of hot absolute alcohol, placed in a vacuum desiccator and set aside in the cold. Straw-colored cubical crystals formed, which were washed with ether containing a little alcohol, and were dried on a porous plate in a desiccator. It melts at 120°, and turns brown on keeping.

| | Calculated. | Found. |
|---|---|---|
| Iodine | 43.58 | 43.2 |

*Picoline Allyl Iodide*, $C_6H_7N.C_3H_5I$.—This preparation is reported by Ramsay,[1] who states: "All the picoline allyl compounds (of which the iodide, chloride, nitrate, sulphate, and oxalate were made) are sirupy liquids," but this seems to be somewhat inaccurate, in that it does not express all the facts.

Allyl iodide was purified by shaking with dilute potash, drying over calcium chloride, and rectifying. When this is mixed with picoline, the colorless liquid rapidly becomes turbid and yellowish oily drops separate. The reaction proceeds readily at ordinary temperatures, and no heating is necessary. It is complete in about an hour, and a light straw-colored sirup is the resulting product. This rapidly becomes brown on standing, but if cooled to 0° solidifies to a yellowish crystalline mass. Recrystallized from small quantity of hot absolute alcohol it yields cubes, transparent and almost colorless. Melting-point 70°.

| | Calculated. | Found. |
|---|---|---|
| Iodine | 48.603 | 48.5 |

*Picoline Hydriodide*, $C_6H_7N.HI$.—Prepared by conducting dry hydriodic acid gas into picoline kept in a freezing-mixture, and drying on a porous plate over sulphuric acid. A white snowy mass which is rather unstable, and separates readily into its proximate constituents, for which reason the melting-point could not be taken. It was also prepared by adding fuming hydriodic acid (sp. gr. 1.96) to picoline kept in a freezing-mixture, and inducing crystallization by means of the previous preparation. This preparation was attempted by Ramsay,[2] but he obtained it only in solution.

[1] *Phil. Mag.*, (5), 2, 279.
[2] *Ibid.*, (5), 2, 271.

| | Calculated. | Found. |
|---|---|---|
| Iodine | 57.41 | 57.62 |

II. PERIODIDES.

*Picoline Hydrogen Diiodide*, $C_6H_7N.HI.I$.—Obtained by adding one equivalent of iodine to one of hydriodide, both in alcohol. As the alcohol evaporates, a dark brown oil separates, which on exposure to low temperatures crystallizes in prisms, dark brown, hard and gritty. The melting-point is about 95° but not sharp.

| | Calculated for $C_6H_7N.HI.I$. | Found. |
|---|---|---|
| Total iodine | 72.94 | 72.5 |
| Additive iodine | 36.47 | 36.25 |

Crystalline bodies of varying composition were also obtained, giving figures of analysis lower than the above, but no definite formula could be ascribed to them except that they were mixtures of $C_6H_7N.HI.I$ with $C_6H_7N.HI$ in varying proportions.

It is worthy of note that *although the hydriodide is unstable, and the odor of picoline is always noticeable about it, the periodides are quite stable, and no odor is perceptible either of picoline or iodine.* A peculiarity of this and all other perhalides of picoline hydriodide or hydrobromide, is that they all become liquid in contact with water, in which, however, they are almost entirely insoluble. Upon standing in a desiccator at low temperature the liquid will again solidify, the composition and properties being unchanged. This fact was observed by Ramsay in connection with the compound described below, but no explanation is offered to account for it.

*Picoline Hydrogen Triiodide*, $C_6H_7N.HI.I_2$.—Dark brown octahedral crystals, melting at 44°. It is prepared by adding two equivalents of iodine to one of hydriodide, both in alcohol. After evaporation of the alcohol the oil that remains is exposed to low temperatures when it crystallizes and is dried on a porous plate.

| | Calculated for $C_6H_7N.HI.I_2$. | Found. |
|---|---|---|
| Total iodine | 80.17 | 79.97 |
| Additive iodine | 53.45 | 53.10 |

A compound was prepared by Ramsay[1] to which he assigns the same formula. He says "when picoline is mixed with strong

[1] *Phil. Mag.*, (5), 2, 273.

aqueous hydriodic acid, and distilled after excess of water has been removed by evaporation, the temperature rises rapidly and the mass turns brown and viscid. If the distillation be continued picoline distils over, and the residue when cool solidifies to a mass of reddish brown needles." These were soluble in alcohol and ether but did not crystallize from them ; were insoluble in carbon disulphide and became liquid in contact with water.

| | Calculated for $C_6H_7N.HI.I_2$. | Calculated for $C_6H_9N.HI.I_2$. | Found. |
|---|---|---|---|
| Total iodine | 80.17 | 79.83 | 80.14 |
| Additive iodine | 53.45 | 53.22 | .... |

The melting-point is given as 79°, and it is evidently a different compound from that obtained by the writer. It is possible that it is from a different one of the isomeric picolines, but to the writer it appears more probable that the compound obtained by Ramsay is a periodide not of picoline but of a hydropicoline. It is known that the pyridine bases are readily reduced to hydrocompounds, and that hydriodic acid is an active reducing agent at high temperatures. In view of this the following equations would show the probable reactions:

$$2HI = 2H + 2I,$$
$$C_6H_7N.HI + 2H + 2I = C_6H_9N.HI.I_2,$$
$$\text{or, } 3C_6H_7N.HI = 2C_6H_7N + C_6H_9N.HI.I_2.$$

This might be proved or disproved by the preparation of the free base from the periodide, but that compound is obtained in such small quantities as to obstruct such a procedure.

*Picoline Hydrogen Pentiodide*, $C_6H_7N.HI.I_4$.—A thick greenish black oil obtained by adding picoline hydriodide to the theoretical amount of alcoholic iodine, and allowing the alcohol to evaporate. The oil was washed with dilute arsenite and with water and dried in a desiccator. It did not solidify at —25°.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 87.08 | 87.12 |
| Additive iodine | 69.66 | 69.58 |

*α-Picoline Methyl Triiodide*, $C_6H_7N.CH_3I.I_2$. — Blue-black feathery plates, melting at 134°. This compound, or rather a mixture of its isomers, was prepared by Ramsay[1] by dissolving iodine in an alcoholic solution of the normal iodide. He says

[1] *Phil. Mag.*, (5), **2**, 278.

that on cooling it crystallized out in bluish-black feathery plates which transmitted red light, and gives the melting-point as 129°. For the preparation of the α-compound, picoline was fractionated very slowly, carefully, and repeatedly, and the fraction boiling at 131.5°–132.5° was used. This was converted into the methiodide, which was crystallized once from absolute alcohol. A portion of this was treated with the theoretical amount of iodine in hot alcohol, heated to dissolve the periodide formed and allowed to crystallize. The periodide was then recrystallized once from absolute alcohol, and found to melt at 134° as given above (preparation I). It was also prepared by adding iodopotassium iodide to an aqueous solution of picoline methyl iodide, keeping the latter in excess. By this means an abundant powdery precipitate is formed, which was washed with water, dried, and found to melt at 133° (preparation II). Recrystallized from alcohol it was identical with I in appearance and melting-point.

It was obtained once as short brown needles, melting at 135° (preparation III), but on subsequent recrystallization it yielded feathery plates.

| | Calculated for $C_6H_7N.CH_3I.I_2$. | (Ramsay) | Found. I. | II. | III. |
|---|---|---|---|---|---|
| Total iodine ..... | 77.81 | 77.59 | 78.10 | 77.54 | 77.62 |
| Additive iodine .. | 51.87 | .... | 52.26 | 51.50 | 52.29 |

*β-Picoline Methyl Triiodide*, $C_6H_7N.CH_3I.I_2$.—β-Picoline was prepared by following the directions of Schwartz[1] in what is usually known as Baeyer's[2] synthesis. A yield of 15 grams was obtained from 220 grams glycerine, 87.5 grams ammonium phosphate, and 175 grams phosphorus pentoxide. This was distilled and collected in three fractions, and each fraction converted into the methiodide, but as none could be obtained crystalline, they were separately converted into the triiodide by addition of the theoretical amount of alcoholic iodine. A number of products were obtained differing in physical properties (oils, plates, needles, etc.), but all gave figures of analysis agreeing with the formula $C_6H_7N.CH_3I.I_2$, and on purification by alcohol and repeated recrystallization were separated into two lots. One of these melted sharply at 134° and agreed in every way with the α-compound described above. The other after several re-

[1] *Ber. d. chem. Ges.*, **24**, 1676; *Chem Centrbl.*, (1891), ii, 172.
[2] *Ber. d. chem. Ges.*, **2**, 398; *Chem. Centrbl.*, (1870), 14.

crystallizations yielded light brown feathery plates, melting at 36°.

These results agree with those of Schwartz, who found that his product contained five per cent. of α-picoline.

| | Calculated for $C_6H_7N.CH_3I.I_2$. | Found. α | β |
|---|---|---|---|
| Total iodine | 77.81 | 78.50 | 77.62 |
| Additive iodine | 51.87 | 51.78 | 51.73 |

*γ-Picoline Methyl Triiodide*, $C_6H_7N.CH_3I.I_2$.—α-Picoline methyl iodide is less soluble in alcohol than its isomers, and the same is true of the corresponding triiodides. A portion of picoline boiling at 137°–140° (the final fraction from a 400 grams lot) was converted into the methiodide and triiodide, and the latter was crystallized from alcohol. The first crops of crystals were the feathery plates of the α-compound, but finally crystals of another kind were seen, very different in color, shape, and appearance, and easily picked out by hand. These were recrystallized and came out as light brown hexagonal plates which melted at 101°. Repeated recrystallizations from alcohol did not alter the melting-point or crystalline form. The same compound was obtained from other fractions of the picoline, and by exclusion it is reasoned that this must be the γ-compound. On account of the small amount obtained it was not studied as thoroughly as could be desired, but there hardly seems reason to doubt its identity.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 77.81 | 78.04 |
| Additive iodine | 51.87 | 51.53 |

*α-Picoline Methyl Pentiodide*, $C_6H_7N.CH_3I.I_4$.—Flat needles, blue-black, melting at 60°. It is prepared by adding the corresponding normal iodide to the theoretical amount of alcoholic iodine, or prepared from the triiodide by boiling with the calculated amount of alcoholic iodine. It is also obtained by adding an aqueous solution of the normal iodide to iodopotassium iodide, keeping the latter in excess.

| | Calculated. | Found. I. | II. |
|---|---|---|---|
| Total iodine | 85.43 | 85.7 | 85.6 |
| Additive iodine | 68.34 | 68.5 | 68.7 |

*β-Picoline Methyl Pentiodide*, $C_6H_7N.CH_3I.I_4$.—A brown-black

oil not solidifying at —25°. Prepared from the corresponding triiodide by boiling with the theoretical amount of alcoholic iodine. The alcohol is then allowed to evaporate, and the oil washed with dilute arsenite and with water, and dried in a desiccator.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 85.43 | 85.62 |
| Additive iodine | 68.34 | 68.44 |

*γ-Picoline Methyl Pentiodide*, $C_6H_7N.CH_3I.I_4$.—Slender steel-blue needles, melting at 63°. It is prepared from the corresponding triiodide by boiling with the calculated amount of alcoholic iodine.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 85.43 | 85.51 |
| Additive iodine | 68.34 | 68.42 |

*α-Picoline Methyl Heptiodide*, $C_6H_7N:CH_3I.I_6$.—Dark green, feathery plates, melting at 57°. It gives off iodine on exposure to air, and pentiodide remains. Prepared by dissolving the calculated amounts of normal iodide and iodine in hot alcohol, and boiling fifteen minutes under reflux condenser. On cooling an oil separates which soon solidifies, and at the same time crystals are formed.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 89.146 | 88.05 |
| Additive iodine | 76.411 | 76.04 |

*γ-Picoline Methyl Heptiodide*, $C_6H_7N.CH_3I.I_6$. Small, flat needles, dark green, melting at 81.5°. It is more stable than the preceding compound. Prepared by treating the corresponding triiodide with the theoretical amount of iodine, and boiling for fifteen minutes under a reflux condenser.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 89.146 | 89.14 |
| Additive iodine | 76.411 | 76.11 |

*α-Picoline Ethyl Triiodide*, $C_6H_7N.C_2H_5I.I_2$.—Dark brown oil, obtained by adding two equivalents or less of iodine to one equivalent of the normal iodide, both in alcohol. The oil is separated, washed with dilute arsenite and with water, and dried in desiccator. It remained liquid at —25°.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 75.70 | 76.10 |
| Additive iodine | 50.47 | 50.62 |

*α-Picoline Ethyl Pentiodide*, $C_6H_7N.C_2H_5I.I_4$.—A green-black oil, obtained by adding one equivalent of normal iodide to four of iodine, both in alcohol. It was washed and dried as the preceding. It did not solidify at —25°.

On standing several weeks at 0° and below, a few crystals formed (about 0.1500 gram). These were very long needles, almost black. Dried on porous plate they were found to melt at 80°, and gave figures of analysis under column II below. This is probably the *γ*-picoline compound.

| | Calculated for $C_6H_7N.C_2H_5I.I_4$. | Found. I. | II. |
|---|---|---|---|
| Total iodine | 83.85 | 83.4 | 82.9 |
| Additive iodine | 67.08 | 67.1 | 66.8 |

*Picoline Propyl Triiodide*, $C_6H_7N.C_3H_7I.I_2$.—Brown oil obtained by adding iodine to normal iodide in theoretical proportions, both in alcohol. It was washed and dried as the preceding. On standing several days at low temperature it crystallized in fine needles, melting at 16°.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 73.65 | 73.45 |
| Additive iodine | 49.10 | 49.07 |

*Picoline Propyl Pentiodide*, $C_6H_7N.C_3H_7I.I_4$.—A green-black oil, obtained by adding normal iodide to alcoholic iodine in proper proportions. It was washed and dried as the preceding. It did not solidify at —25°.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 82.32 | 82.1 |
| Additive iodine | 65.86 | 65.7 |

*Picoline Isopropyl Diiodide*, $C_6H_7N.C_3H_7I.I$.—Light brown cubes, melting at 106°. Obtained as the final crop of crystals from the addition of one equivalent of iodine to one of normal iodide. The triiodide is formed at the same time, and in larger quantity, and is separated in crystallization. The diiodide appears to be rather unstable, its alcoholic solution passing to triiodide on warming. The diiodide was also obtained from a portion of normal iodide, containing some alcohol, that had been allowed to stand for about a year, when it was observed that the

sirupy liquid had become brown and crystals had been deposited. These were collected, dried on a porous plate, and recrystallized from alcohol without heating.

| | Calculated for $C_6H_7N.C_3H_7I.I_2$. | Found. I. | II. |
|---|---|---|---|
| Total iodine | 65.076 | 65.10 | 64.82 |
| Additive iodine | 32.538 | 32.61 | 32.51 |

*Picoline Isopropyl Triiodide*, $C_6H_7N.C_3H_7I.I_2$.—Light brown needles, long and silky, melting at 60°. They are formed when alcoholic iodine is mixed with a solution of normal iodide in any proportion. It is readily prepared free from admixture by mixing in theoretical proportions and allowing to crystallize.

| | Calculated for $C_6H_7N.C_3H_7I.I_2$. | I. | Found. II. | III. |
|---|---|---|---|---|
| Total iodine | 73.65 | 72.78 | 73.74 | 73.01 |
| Additive iodine | 49.10 | 48.66 | 49.18 | 48.9 |

*Picoline Isopropyl Pentiodide*, $C_6H_7N.C_3H_7I.I_4$.—Greenish black oil, liquid at —25°. It was obtained by adding normal iodide to the calculated amount of iodine in alcohol, and boiling a few minutes under a reflux condenser. When cold the oil is separated, washed, and dried as in previous preparations.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 82.33 | 82.40 |
| Additive iodine | 65.86 | 65.77 |

*Picoline Butyl Triiodide*, $C_6H_7N.C_4H_9I.I_2$.—Light brown needles, long and flat, melting at 33°. They were prepared by adding iodine to the normal iodide in proper proportions, both in alcohol, and allowing to crystallize at low temperature.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 71.70 | 71.81 |
| Additive iodine | 47.80 | 47.82 |

*Picoline Butyl Pentiodide*, $C_6H_7N.C_4H_9I.I_4$.—Dark brown oil, not solidifying at —20°. Formed by adding normal iodide to alcoholic iodine in proper proportions.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 80.856 | 81.01 |
| Additive iodine | 64.685 | 64.67 |

*Picoline Isobutyl Triiodide*, $C_6H_7N.C_4H_9I.I_2$.—Prepared from the normal iodide in the usual manner. It is a dark brown oil, not solidifying at —15°.

| | Calculated | Found. |
|---|---|---|
| Total iodine | 71.705 | 71.56 |
| Additive iodine | 47.803 | 48.04 |

*Picoline Isobutyl Pentiodide*, $C_6H_7N.C_4H_9I.I_4$.—A brown-black oil, not solidifying at —20°. It was prepared from the normal iodide by adding it to alcoholic iodine in proper proportions and boiling under reflux condenser for a few minutes.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 80.856 | 80.95 |
| Additive iodine | 64.685 | 64.73 |

*Picoline Secondary Butyl Triiodide*, $C_6H_7N.C_4H_9I.I_2$.—Brown oil, not solidifying at 0°. It was prepared in the usual manner from the normal iodide previously described. The picoline hydrogen periodide which accompanies it is much more soluble in alcohol, so that as the alcohol evaporates the butyl periodide separates out first, and quite pure. This also applies to the pentiodide described next.

| | Calculated for $C_6H_7N.C_4H_9I.I_2$. | Found. I. | Found. II. |
|---|---|---|---|
| Total iodine | 71.705 | 71.56 | 71.63 |
| Additive iodine | 47.803 | 48.04 | 47.92 |

*Picoline Secondary Butyl Pentiodide*, $C_6H_7N.C_4H_9I.I_4$.—A green-black oil, not solidifying at 0°. It was obtained in the usual manner from the normal iodide.

| | Calculated for $C_6H_7N.C_4H_9I.I_4$. | Found. I. | Found. II. |
|---|---|---|---|
| Total iodine | 80.856 | 80.73 | 81.21 |
| Additive iodine | 64.685 | 64.56 | 64.77 |

*Picoline Tertiary Butyl Salts* are not formed. (See preceding part of this paper under normal iodides.)

*Picoline Isoamyl Diiodide*, $C_6H_7N.C_5H_{11}I.I$. — Light brown plates, melting at 96°. They were prepared from the normal iodide previously described by adding alcoholic iodine in theoretical quantity. The triiodide is formed at the same time and crystallizes out first.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 60.71 | 60.35 |
| Additive iodine | 30.355 | 30.12 |

*Picoline Isoamyl Triiodide*, $C_6H_7N.C_5H_{11}I.I_2$.—Light brown, overlapping plates, melting at 22°. They are obtained when-

ever alcoholic iodine is mixed with normal iodide. Prepared pure by mixing in theoretical quantities, and allowing to crystallize at low temperature.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 69.86 | 69.5 |
| Additive iodine | 46.57 | 46.3 |

*Picoline Isoamyl Pentiodide*, $C_6H_7N.C_5H_{11}I.I_4$.—Brown-black oil, not solidifying at —25°. It was obtained by mixing alcoholic iodine with normal iodide in theoretical proportions, and boiling a few minutes under reflux condenser.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 79.44 | 80.1 |
| Additive iodine | 63.55 | 63.3 |

*Picoline Allyl Triiodide*, $C_6H_7N.C_3H_5I.I_2$.—Purplish brown needles, melting at 62°. Also obtained as light brown feathery plates, of same composition and melting-point, which on recrystallization came out as needles. It is obtained as an oil by adding iodine to the normal iodide in theoretical proportions. On cooling to 0° the oil solidifies, is dried on a porous plate and recrystallized, coming out as above. Ramsay[1] states that no diiodide of the allyloiodide was obtained, but goes on to say that by adding iodine to the normal iodide he obtained an oil, insoluble in carbon disulphide, and from which this solvent does not extract iodine. He reports no analysis of it.

| | Calculated. | Found. |
|---|---|---|
| Total iodine | 73.94 | 73.875 |
| Additive iodine | 49.29 | 49.25 |

*Picoline Allyl Pentiodide*, $C_6H_7N.C_3H_5I.I_4$.—A green-black oil, not solidifying at —25°. It was obtained by adding normal iodide to alcoholic iodine in proper proportions, and heating a short time under reflux condenser.

| | Calculated | Found. |
|---|---|---|
| Total iodine | 82.35 | 82.25 |
| Additive iodine | 65.88 | 65.76 |

### III. NORMAL CHLORIDES.

*Picoline Hydrochloride*, $C_6H_7N.HCl.\frac{1}{2}H_2O$.—Prepared by Anderson[2] in 1846, and again by Ramsay[3] in 1876, but no analyses

[1] *Phil. Mag.*, (5), **2**, 279.
[2] *Ibid.*, (4), **9**, 145 and 214; *Ann. Chem.* (Liebig), **60**, 86.
[3] *Phil. Mag.*, (5) **2**, 271.

are reported by either. White crystals, extremely deliquescent, very stable, and sublime or distil unchanged except for loss of water. Prepared by acidifying picoline with hydrochloric acid and distilling after excess of water has been expelled; or water can be expelled, and the residue which remains on cooling is dried on porous plates in a vacuum desiccator.

Preparation I was made by acidifying picoline with concentrated hydrochloric acid, evaporating to a thick sirup and allowing to crystallize in desiccator. Crystals were dried on a porous plate in the desiccator, and analyzed. Preparation II is the same, allowed to remain two weeks in the desiccator. Preparation III is the same heated for several hours at 110°, when it was observed that the compound was liquid, and a large part of it had sublimed away. The remainder was cooled in a desiccator and analyzed.

| | Calculated for $C_6H_7N.HCl.\frac{1}{2}H_2O$. | $C_6H_7N.HCl$. | Found. I. | II. | III. |
|---|---|---|---|---|---|
| Chlorine .. | 25.58 | 27.36 | 25.42 | 25.60 | 26.81 |

The melting-point given by Anderson is 160°, but this is only partially verified. Preparation I melted at 165°; II became liquid at 168°, but did not melt to a clear liquid until a temperature of 198° was reached; III became liquid at 80° and cleared up at 85°. From this it would appear that the melting-point of the *hydrated* salt is about 200°, and of the *anhydrous* about 80°, certainly a very remarkable difference.

*α-Picoline Methyl Chloride*, $C_6H_7N.CH_3Cl.H_2O$.—Prepared by Ramsay[1] by treating picoline methyl iodide in aqueous solution with freshly precipitated silver chloride. On evaporation to dryness a white, crystalline, deliquescent mass was obtained. No analysis or melting-point was reported. When prepared in this manner, crystallized once from absolute alcohol, and dried on a porous plate in a vacuum desiccator it was found to melt in the neighborhood of 70°, but not sharply, on account of its great hygroscopic power. The crystals contain one molecule of water of crystallization.

| | Calculated for $C_6H_7N.CH_3Cl.H_2O$. | $C_6H_7N.CH_3Cl$. | Found. |
|---|---|---|---|
| Chlorine ..... | 21.94 | 23.045 | 21.72 |

[1] *Phil. Mag.*, (5), 2, 277.

IV. NORMAL BROMIDES.

*Picoline Hydrobromide*, $C_6H_7N.HBr$.—Prepared by Ramsay[1] in the same manner as the hydrochloride, and also by brominating picoline and distilling the resulting oil. It was prepared by the writer by conducting dry gaseous hydrobromic acid into picoline, and drying in a desiccator on porous plates. It recrystallized from a very small quantity of absolute alcohol (preparation I) and formed very deliquescent white crystals, melting at 187° (Ramsay). At 306° the compound distils unchanged, coming over as a thick viscid sirup, which on standing in a desiccator gradually solidifies (preparation II).

| | Calculated for $C_6H_7N.HBr$. | Found. I. | II. |
|---|---|---|---|
| Bromine | 45.94 | 45.06 | 46.27 |

*Picoline Methyl Bromide*, $C_6H_7N.CH_3Br$.—Prepared by conducting methyl bromide into picoline. Union takes place readily, with evolution of some heat, and the product soon solidifies to a flesh-colored mass. This was dried on porous plates *in vacuo* over sulphuric acid to remove excess of picoline, and recrystallized from a small quantity of absolute alcohol. It forms long colorless needles, which on keeping gradually turn pink. It melts at 217°.

| | Calculated. | Found. |
|---|---|---|
| Bromine | 42.52 | 42.47 |

*Picoline Ethyl Bromide*, $C_6H_7N.C_2H_5Br$.—Prepared by heating the constituents together under a reflux condenser. The formation is not as ready as with the corresponding iodide, but the union is complete in three or four hours. On standing in the cold it gradually solidifies, and is crystallized from a small quantity of absolute alcohol, from which it comes out as transparent colorless crystals. It is somewhat deliquescent and is dried on a porous plate in a desiccator. It melts at 97°.

| | Calculated. | Found. |
|---|---|---|
| Bromine | 39.56 | 38.9 |

V. PERBROMIDES.

*Picoline Hydrogen Dibromide*, $C_6H_7N.HBr.Br$.—Red rhombohedral crystals, melting at 76°. It was prepared by mixing the normal hydrobromide with the corresponding tribromide in equi-

[1] *Phil. Mag.*, (5), 2, 271.

molecular proportions, in presence of a small amount of absolute alcohol. On standing the dibromide crystallizes out and is dried on porous plates.

| | Calculated. | Found. |
|---|---|---|
| Total bromine | 62.95 | 62.2 |
| Additive bromine | 31.47 | 31.1 |

*Picoline Hydrogen Tribromide*, $C_6H_7N.HBr.Br_2$.—Transparent oil, deep red in color, not solidifying at —15°. It was prepared by adding bromine to an aqueous solution of the hydrobromide, or by aspirating vapors of bromine through the same.

| | Calculated for $C_6H_7N.HBr.Br_2$. | Ramsay's analyses. | | Found. |
|---|---|---|---|---|
| Total bromine | 72.00 | 71.17 | 68.04 | 72.74 |
| Additive bromine | 48.00 | ... | .... | 48.21 |

Ramsay[1] describes a compound to which he assigns the same formula, and which he obtained by heating the constituents in a sealed tube to 190°, and also by adding bromine to a solution of the hydrobromide. His compound crystallized from hot water in yellow crystals, melting at 85° with loss of bromine. The second method could not be verified, and the first was not tried by the writer. Picoline hydrogen tribromide should melt lower than the corresponding triiodide (44°); and if a solid, should be liquefied by water. In view of these and other facts it appears that Ramsay must have had quite a different compound, perhaps $C_6H_6BrN.HBr.Br_2$, which although differing in empirical formula by only one hydrogen atom would have properties very different from the compound obtained by the writer.

*α-Picoline Methyl Tribromide*, $C_6H_7N.CH_3Br.Br_2$.—When vapors of bromine are aspirated through an aqueous solution of picoline methyl bromide to saturation, a red oil is precipitated, which soon solidifies. On recrystallizing from alcohol it comes out as orange-yellow plates, melting at 111°, and having a faint odor of bromine.

| | Calculated for $C_6H_7N.CH_3Br.Br_2$. | Found. I. | II. |
|---|---|---|---|
| Total bromine | 68.94 | 67.99 | 69.21 |
| Additive bromine | 45.96 | 45.50 | 45.42 |

*Picoline Ethyl Tribromide*, $C_6H_7N.C_2H_5Br.Br_2$.—On aspirating vapors of bromine through an aqueous solution of picoline ethyl

[1] *Phil. Mag.*, (5), 2, 275.

bromide, a transparent deep red oil separates as before, but in this case it remains liquid in a freezing-mixture.

| | Calculated. | Found. |
|---|---|---|
| Total bromine | 66.26 | 66.34 |
| Additive bromine | 44.17 | 44.22 |

VI. IODOBROMIDES.

*Picoline Hydriodide Bromide*, $C_6H_7N.HI.Br$.—Dark red crystals, melting at 68°. Prepared by mixing equimolecular portions of picoline hydriodide and picoline hydriodide dibromide; or of picoline hydrogen diiodide with the corresponding dibromide, in presence of a small quantity of absolute alcohol.

| | Calculated for $C_6H_7N.HI.Br$. | Found. |
|---|---|---|
| Total halogens | 68.726 | 68.57 |
| Total iodine | 42.156 | 41.93 |
| Total bromine | 26.570 | 26.64 |
| Additive halogen (bromine) | 26.570 | 26.72 |

*Picoline Hydriodide Dibromide*, $C_6H_7N.HI.Br_2$.—Dark red crystals melting at 58°. It was obtained in a number of ways. I. Two molecular portions of tribromide and one of triiodide were mixed in presence of a small quantity of absolute alcohol. II. Picoline is diluted with water and acidified with hydrobromic acid, potassium iodide is added and vapors of bromine are aspirated through to saturation. By this means a red oil is obtained which solidifies to a crystalline mass, and melts at 57°. III. Vapors of bromine were aspirated through water in which was suspended picoline hydrogen diiodide. Red crystals were obtained, melting at 48°.

| | Calculated for $C_6H_7N.HI.Br_2$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Total halogens | 75.295 | 74.08 | 75.47 | 73.45 |
| " iodine | 33.31 | 29.09 | 29.63 | 21.99 |
| " bromine | 41.985 | 44.82 | 45.50 | 51.29 |
| Additive halogen | 41.985 | 42.15 | 41.94 | 42.21 |
| Atomic ratio, I : Br | 1 : 2 | 1 : 2.4 | 1 : 2.4 | 1 : 3.7 |

*α-Picoline Methyl Iodide Dibromide*, $C_6H_7N.CH_3I.Br_2$.—When vapors of bromine are aspirated through an aqueous solution of picoline methyl iodide (or any normal iodide), the first thing noticed is a brownish precipitate, evidently a triiodide, resulting from the displaced iodine which *immediately* combines with the

normal iodide still in excess. As the process is continued the precipitate becomes lighter in color (due to its conversion into iodobromide), and the supernatant liquid becomes clear. A portion of the precipitate was removed at this point and recrystallized from alcohol (I), and the remainder further treated with bromine for a considerable time and then recrystallized (II). I melted at 121°, and II at 110°.

That the triiodide is converted into iodobromide was shown by suspending it in water and aspirating vapors of bromine through it for some time. The product was then crystallized from alcohol and yielded fine orange-red needles, melting at 121° (III).

Prepared purest and best by mixing two molecular portions of tribromide with one of triiodide, and crystallizing from alcohol. Slender orange-red needles formed, two to three inches long, melting at 121.5° (IV).

| | Calculated for $C_6H_7N\,CH_3I.Br_2$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| Total halogens..... | 72.630 | 71.46 | 70.35 | 70.21 | 71.83 |
| " iodine ..... | 32.136 | 27.36 | 18.02 | 16.30 | 31.70 |
| " bromine ..... | 40.494 | 43.90 | 51.71 | 53.91 | 40.28 |
| Additive halogen ... | 40.494 | 40.87 | 40.53 | 40.50 | 40.48 |
| Atomic ratio I : Br .. | 1 : 2 | 1 : 2.2 | 1 : 4.5 | 1 : 5.2 | 1 : 2 |

The compound is perfectly stable and does not decompose at 220°, although a faint odor of bromine is usually noticeable in the bottle.

On gently warming a solution of potassium iodide, in which is suspended any one of the above preparations, the orange-red color immediately disappears, and the crystals become brown. Recrystallized from alcohol they then melt at 133°.

| | Calculated for $C_6H_7N.CH_3I.I_2$. | Found. |
|---|---|---|
| Total iodine ..... | 77.81 | 77.63 |
| Additive iodine ..... | 51.87 | 51.20 |

*α-Picoline Methyl Iodide Iodobromide*, $C_6H_7N.CH_3I.IBr$.—Long, flat, interlaced needles, reddish brown in color, melting at 113°. It was prepared by mixing two molecular portions of $\alpha$-$C_6H_7N.CH_3I.I_2$, with one of $\alpha$-$C_6H_7N.CH_3Br.Br_2$ and crystallizing from hot alcohol.

| | Calculated for $C_6H_7N.CH_3I.IBr$. | Found. |
|---|---|---|
| Total halogen | 75.525 | 75.53 |
| " bromine | 18.097 | 18.15 |
| " iodine | 57.428 | 57.24 |
| Atomic ratio I : Br | 2 : 1 | 2 : 1 |

*Picoline Allyl Iodide Dibromide*, $C_6H_7N.C_3H_5I.Br_2$.—Orange-yellow plates, melting at 84°, perfectly stable and odorless. It was prepared by aspirating bromine through an aqueous solution of the normal iodide, and crystallizing from alcohol. The allyl group does not become saturated by the bromine.

| | Calculated for $C_6H_7N.C_3H_5I.Br_2$. | Found. |
|---|---|---|
| Total halogen | 68.13 | 68.27 |
| " bromine | 37.99 | 38.15 |
| " iodine | 30.14 | 29.93 |

## VII. AMINE PERHALIDES.

*Picoline Dibromide*, $C_6H_7N.Br_2$.—These compounds were prepared by Ramsay,[1] and are given here for the sake of completeness. The dibromide is formed by addition of bromine to picoline in chloroform, and evaporating the chloroform in a vacuum desiccator. Small interlaced needles formed which lose bromine on standing.

*Picoline Iodochloride*, $C_6H_7N.ICl$.—Prepared by Ramsay[1] in the same manner as the preceding by adding iodine chloride to picoline in chloroform. Long yellow needles formed.

*Picoline Periodide*, $C_6H_7N.I_x$.—The existence of compounds analogous to pyridine tetriodide is indicated, although they were not obtained by the writer in a pure form. It is well known that a solution of iodine in chloroform is violet. If now a drop of picoline be added, the color at once changes to brown. On allowing the chloroform to evaporate, a thick sirup remained, but crystals were not obtained.

## DISCUSSION.

The compounds described in the preceding pages are in every way analogous to those of pyridine, and with few exceptions agree with generalizations based upon a study of the pyridine compounds.[2]

[1] *Phil. Mag.*, (5). 2, 275.

[2] Prescott: Pyridine Alkyl Iodides, This Journal, 18, 91.

In each case where a melting-point could be taken, the normal iodides of picoline were found to melt higher than the corresponding pyridine compound, and the same is generally but not invariably true of the periodides. Also, the addition-products with methyl bromide follow the rule, but the reverse is true with ethyl bromide; while the other normal bromides and chlorides do not give melting-points sufficiently sharp for comparison. The relation existing between the boiling-points of the alkyl iodides and the melting-points of their pyridine addition-products is found to hold true with picoline in all cases except the isopropyl, amyl, and various butyl compounds, in which cases the melting-points are more or less anomalous.

The generalizations of Carnally[1] in regard to isomeric compounds were found to apply in nearly all instances. These are: "Of two isomers, that is most soluble which has the lower melting-point." "Of two or more isomeric compounds, those whose atoms are the most symmetrically or compactly arranged, melt higher than those in which the arrangement is asymmetric or in long chains." "Those compounds melt highest which have the greatest number of side chains; and compactness sometimes overbalances increase in atomic weight." Exceptions to these are observed in the case of the butyl and isobutyl compounds, both normal and superiodides. Also, compounds of $\gamma$-picoline should melt highest of the three isomers, but this is not the case with the methyl triiodides, and probably not with the normal methiodide.

From a practical or analytical point of view, perhaps the most important result of this research is the separation or the identification of the three isomeric picolines by means of their methyl triiodides. The separation has not been studied in all its aspects and possibilities on account of the scarcity of material and difficulty of preparation of the $\beta$- and $\gamma$-picolines. The picoline drawn upon for the preceding preparations was a Kahlbaum article, boiling at 130°–134°. It consisted very largely of $\alpha$-picoline, but contained some pyridine and some $\gamma$-picoline. The larger part distilled over between 131° and 133°, but on slow and careful fractionation a small amount (six grams from a 400 grams

[1] *Phil. Mag.*, (5), **13**, 116 and 180; *J. Chem. Soc.*, **53**, 782.

lot) was obtained which boiled at 137°–140°, and yielded the γ-picoline compounds previously described.

At present there is no ready method of obtaining the tertiary base in this series after it has once combined with an alkyl iodide to form a salt of the quaternary base, for on distilling the hydroxide of the quaternary base decomposition takes place, the ring is broken down and an aliphatic amine is produced, along with other products of decomposition, and no odor of picoline could be detected in the distillate. The use of the method as a *separation* is therefore diminished, but it is promising as a means of identification of the picolines.

In regard to the conditions of formation of the various periodides, it appears that the lower periodides (usually a triiodide) are formed whenever iodine is added to a normal iodide, or when the iodine is not in excess; and that the pentiodides are formed whenever these conditions are reversed. For formation of the heptiodides it is necessary to boil for some time with a considerable excess of iodine. The heptiodides are unstable, giving off iodine on standing and becoming pentiodides. The diiodides are also unstable (except $C_6H_7N.HI.I$) as on boiling their alcoholic solutions they change to triiodides and normal iodides.

In solution the additive halogens are very reactive, and rearrange themselves with the greatest readiness. Lower periodides take up more iodine and change to pent- and heptiodides on boiling with alcoholic iodine; and these can be changed to triiodides with equal readiness by boiling with normal iodide. This readiness of rearrangement is most noticeable in the case of the complex perhalides, and was studied thoroughly in connection with the picoline methyl- and allyl-iodobromides.

The study of the complex perhalides, those with more than one halogen element, is of interest as bearing upon questions of constitution and the structural character of the halogens. When solutions of a periodide and a perbromide are mixed, or when a mixture of the two is dissolved in alcohol, reaction appears to be instantaneous, and an iodobromide results. The iodobromides are isomorphous with the perbromides, and if the latter be in excess it will crystallize out with the iodobromide in homogeneous crystals, so that different products may vary widely in composition, and yet be identical in appearance and even in

melting-point. The same results are obtained when bromine is aspirated through a solution of normal iodide or through a suspension of a periodide. At one time the question was raised in this research whether the complex perhalides were not in reality *mixtures* of the *simple* perhalides, but this now appears to be improbable. In view of these conclusions it will be seen that isomerism in the arrangement of the halogens is impossible, and that of the two formulas $C_6H_7N.CH_3I.Br_2$ and $C_6H_7N.CH_3Br.IBr$ only one can exist, and only one such compound is known.

The proof of the structure of the complex perhalides is perhaps not complete, but from a careful consideration of the facts at hand, the writer takes the view that *in every case it is the halogen of higher atomic weight that is next to the nitrogen.* The facts bearing on this question are as follows :

1. The great ease of formation and stability[1] of the periodides, and the power of iodine to hold a large number of additive atoms of iodine.[2]

2. The non-existence[3] of perchlorides.

3. The intermediate position of perbromides; the limit of the number of additive atoms being usually two, but in some cases four[2] atoms of bromine.[4]

4. Iodobromides are more stable than perbromides.

5. Iodine displaces bromine or chlorine completely, and bromine displaces chlorine completely,[5] a reversal of the usual reactions of these elements ; while bromine or chlorine displaces *all but one* of the iodine atoms in the molecule, and chlorine displaces *all but one* of the bromine atoms.

Since no perchlorides are formed, chlorine cannot hold chlorine, and the formula $C_5H_5\overset{H}{\underset{|}{N}} : Cl\langle \overset{I}{\underset{Cl}{||}}$ is untenable, and the compound of that composition would have the constitution

$$C_5H_5\overset{H}{\underset{|}{N}}-I\langle \overset{Cl}{\underset{Cl}{||}} \quad \text{or} \quad C_5H_5\overset{H}{\underset{|}{N}}-I\langle \begin{matrix} Cl \\ Cl \end{matrix}.$$

[1] See under Picoline Hydrogen Diiodide, in previous part of this paper.

[2] Atropine Enneaiodide, $C_{17}H_{23}NO_3.HI.I_8$, Prescott and Gordin: This Journal, 20, 711.

[3] Trowbridge and Diehl: This Journal, 19, 571.

[4] Quinoline Hydrogen Pentabromide, $C_9H_7N.HBr.Br_4$, Trowbridge : This Journal, 21, 68.

[5] Trowbridge and Diehl: This Journal, 20, 563.

The general properties of these periodides and perhalides are much the same as those of the corresponding pyridine compounds. All the pentiodides, except two of the picoline methyl pentiodides are oils, while the triiodides with few exceptions are nicely crystalline. They are all insoluble in water, but are soluble in alcohol or chloroform. They are soluble in hot solutions of alkali carbonates without color (formation of iodate and iodide), and from such solution they are reformed and precipitated by addition of acids. They are soluble in caustic alkalies with more or less decomposition ; and on boiling with alkalies iodoform appears to be formed. Normal halides of the tertiary base (picoline hydrochloride) are decomposed by solutions of alkali bicarbonates, yielding the free base. Solutions of potassium iodide convert all perhalides to pure periodides. The perhalides of the quarternary base are in general very stable, and some of the liquid periodides may be boiled for hours with decinormal arsenite before solution takes place.

## METHODS OF ANALYSIS.

In analyzing the compounds described, volumetric processes were used almost exclusively, although the results were checked frequently by gravimetric estimations.

### I. ANALYSIS OF COMPOUNDS CONTAINING ONLY ONE HALOGEN.

For estimating halogens in the normal halides, the Volhard method was used, precipitating with decinormal silver nitrate and retitrating with thiocyanate. The volumetric silver solution was standardized and tested at intervals by precipitating a definite portion and weighing the silver chloride formed.

In perhalides containing only one halogen, the additive or exterior halogen, was estimated with decinormal arsenious acid in sodium bicarbonate, retitrating with iodine. The arsenite was made by weighing resublimed arsenic, dissolving in sodium bicarbonate and when cold diluting to required volume. Arsenite has this advantage over thiosulphate, that both the arsenate and arsenite of silver are soluble in nitric acid, so that there are no products of reaction to interfere with the estimation by the Volhard method of the total halogen present in the same solution. When thiosulphate is used there are products which do interfere.

For estimating the total halogen, the easiest and most rapid method is to dissolve the perhalide in alkaline arsenite, with or without the aid of alcohol, precipitate with decinormal silver nitrate, and titrate the excess of silver with thiocyanate. This was compared with the zinc dust reduction and found to give identical results, with the advantage that no filtering is necessary.

The method of analysis for both additive and total halogen in a simple periodide or perbromide is as follows: A weighed portion is covered with about 10 cc. of alcohol, and decinormal arsenite is added till the perhalide is dissolved and the color destroyed, and the excess of arsenic is titrated with iodine in the ordinary way using starch paste as an indicator. The difference, multiplied by the decinormal factor of the halogen gives the weight of *additive halogen* present in the original sample.

After the titration with iodine, the total halogen can be estimated in the same portion, provided it is known how much iodine was added in the first titration. For this purpose a convenient solution is made by dissolving 12.685 grams iodine and 24.8925 grams potassium iodide in a small amount of water, and diluting to one liter. One cc. of this solution, reduced with arsenic, is equal to two and five-tenths cc. of decinormal silver nitrate, or in other words the solution is decinormal to arsenic and fourth-normal to silver.

### II. ANALYSIS OF MIXTURES OF TWO HALOGEN ELEMENTS.

When two halogens are present, their separate estimation is not quite so easy, but may be accomplished in the following manner: A weighed portion of the complex perhalide is reduced with zinc dust or arsenic as preferred, or any compound containing two halogens, is converted to the condition of a soluble iodide, etc. The halides in the clear solution or filtrate are precipitated with a known amount of standard silver nitrate, the precipitate is collected in the usual manner and weighed, and the filtrate containing the excess of silver is titrated with thiocyanate. By means of the following formulas the percentages are calculated.

Given:

$a$ = weight of substance taken for analysis.

$b$ = weight of silver halides obtained.

$c$ = no. of cc. of $\frac{N}{10}$ silver nitrate required.

To find:

$p$ = percentage of total halogen.

$r$ = atomic ratio of halogens.

$p'$ = percentage of one halogen.

$p'' = p - p'$ = percentage of the other halogen.

For iodine and bromine the formulas are:

$$p = \frac{100\,b - 1.0792\,c}{a} \qquad [1]$$

$$r = \frac{0.023477\,c - b}{b - 0.018787\,c} = \frac{\text{atoms of bromine}}{\text{atoms of iodine}} \qquad [2]$$

$$p' = \frac{126.85\,(b - 0.018787\,c)}{0.469\,a} = \text{per cent. iodine} \qquad [3]$$

$$p'' = \frac{79.95\,(0.023477\,c - b)}{0.469\,a} = \text{per cent. bromine} \qquad [4]$$

For iodine and chlorine they are:

$$r = \frac{0.023477\,c - b}{b - 0.014337\,c} = \frac{\text{atoms of chlorine}}{\text{atoms of iodine}} \qquad [2a]$$

$$p' = \frac{126.85\,(b - 0.014337\,c)}{0.914\,a} = \text{per cent. iodine} \qquad [3a]$$

$$p'' = \frac{35.45\,(0.023477\,c - b)}{0.914\,a} = \text{per cent. chlorine} \qquad [4a]$$

For bromine and chlorine they become:

$$r = \frac{0.018787\,c - b}{b - 0.014337\,c} = \frac{\text{atoms of chlorine}}{\text{atoms of iodine}} \qquad [2b]$$

$$p' = \frac{79.95\,(b - 0.014337\,c)}{0.445\,a} = \text{per cent. bromine} \qquad [3b]$$

$$p'' = \frac{35.45\,(0.018787\,c - b)}{0.445\,a} = \text{per cent. chlorine} \qquad [4b]$$

The deduction of the formulas for iodine and bromine is as follows :

Let $m$ = weight of silver in $b$

$n$ = weight of halogen in $b$

$m + n = b$

$m = 0.010792\,c$

$n = b - m = b - 0.010792\,c$

but $a : n :: 100 : p$

or $$p = \frac{100\,n}{a} = \frac{100\,b - 1.0792\,c}{a} \qquad [1]$$

Also let $w$ = combining weight of mixed halogens.

$x$ = number of atoms of iodine in one molecule of $a$.

$y$ = " " " " bromine in one " " $a$

$r = \frac{y}{x}$ = atomic ratio of bromine to iodine.

then $$w = \frac{126.85\,x + 79.95\,y}{x + y} = \frac{126.85 + 79.95\,r}{1 + r}$$

$$r = \frac{126.85 - w}{w - 79.95}$$

but $m : n :: 107.92 : w$

or $$w = \frac{107.92\,n}{m} = \frac{107.92\,(b - 0.010792\,c)}{0.010792\,c}$$

$$w = \frac{10000\,(b - 0.010792\,c)}{c} = \frac{10000\,b}{c} - 107.92$$

$$r = \frac{234.77 - 10000\,b}{10000\,b - 187.87\,c} = \frac{0.023477\,c - b}{b - 0.018787\,c} \qquad [2]$$

Also:

$0.010792\left(\frac{1}{1+r}\right)c$ = weight of silver combined with iodine in $b$

$0.010792\left(\frac{r}{1+r}\right)c$ = " " " " " bromine " $b$

then $\frac{0.012685\,c}{1+r}$ = " " iodine in $b$ or in $a$

$$\frac{0.007995\,cr}{1+r} = \text{weight of bromine in } b \text{ or in } a$$

$$p' = \frac{100}{a} \times \frac{0.012685\,c}{1+r} = \frac{126.85\,(b - 0.018787c)}{0.469\,a} \quad [3]$$

$$p'' = \frac{100}{a} \times \frac{0.007995\,cr}{1+r} = \frac{79.95\,(0.023477\,c - b)}{0.469\,a} \quad [4]$$

In conclusion profound thanks are expressed to Prof. A. B. Prescott, in whose laboratory and under whose supervision the work has been done.

CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN,
ANN ARBOR, June 9, 1899.

## THE DETERMINATION OF NICKEL IN NICKEL-STEEL.

BY GEO. WM. SARGENT.

Received July 17, 1899.

THE results obtained in this laboratory by the following method have been such as to warrant my placing it before fellow-chemists, who, I believe, will find the method more reliable and more pleasant to work than most procedures now in vogue for the determination of nickel in steel.

The method in detail is as follows: Dissolve two grams of the steel in hydrochloric acid (1.1 sp. gr.), add one cc. of strong nitric acid to oxidize the iron, and evaporate to hard dryness. Take up the residue in twenty cc. hydrochloric acid (1.1 sp. gr.), evaporate to ten cc. volume, and transfer the solution to a 250 cc. separatory funnel.[1] Use warm hydrochloric acid (1.1 sp. gr.) for washing the contents of the beaker into the funnel, taking care to keep the volume as small as possible. Cool the funnel and its contents under the spigot, then introduce forty cc. of ether free from alcohol, which has just been thoroughly shaken with five cc. of strong hydrochloric acid, and shake vigorously for ten minutes, keeping the temperature from rising by frequently holding the funnel under the running water. Allow the funnel to stand a few minutes, draw off the lower aqueous layer containing the nickel, copper, manganese, and other chlorides not held by the ether, wash down the sides of the separatory funnel with hydrochloric acid (1.1 sp. gr.), shake with the

[1] See method of Chase for the "Determination of Nickel and Aluminium in Steel" in the appendix of "The Chemical Analysis of Iron," by Blair, third edition.

ether, and run the washings into the beaker with the chlorides of nickel, copper, etc. Two washings with five to ten cc. of hydrochloric acid are sufficient to completely remove the nickel and other chlorides from the funnel. The ethereal solution containing the ferric chloride is run into a residue bottle and later the ether recovered by distillation. Boil the liquid containing the nickel to completely expel the ether and add to the boiling solution, diluted to at least 200 cc. an excess of ammonia and ten to twenty drops of bromine water, to precipitate any iron or manganese. Filter, wash, redissolve in hydrochloric acid, reprecipitate with ammonia and bromine water, and filter. Combine the filtrates, boil, remove any precipitate, acidulate with hydrochloric acid, boil until the excess of bromine has been expelled, and precipitate the copper as sulphide. The filtrate from the copper sulphide which contains nickel only, is evaporated to a volume of 100 cc., cooled and one cc. excess of ammonia added. Now introduce into the nickel solution, which is best contained in an Erlenmeyer flask, five cc. of silver nitrate (one-half gram silver nitrate in a liter of water), and the same amount of a two per cent. solution of potassium iodide. Run into the opalescent solution, which should have a temperature slightly lower than that of the hand, standard potassium cyanide (one cc. equal to about 0.001 gram of nickel) until the liquid becomes clear and bright. This titration is best made with a black background, when the end-reaction becomes very sharp and decided after a little practice, half a drop only being sufficient to discharge the opalescence.[1]

The potassium cyanide solution is standardized by introducing into an Erlenmeyer flask ten cc. of a solution containing a known amount of recrystallized nickel nitrate, $Ni(NO_3)_2.6H_2O$, ten cc. of hydrochloric acid (1.1 sp. gr.), one cc. excess of ammonia, five cc. each of the silver nitrate and potassium iodide, diluting the whole to 100 cc., and running in the potassium cyanide until the solution clears. It is necessary that a blank be made upon the silver nitrate and potassium iodide used as the indicator, under the same conditions as the standardization, and this amount deducted from each titration.

[1] See "Determination of Nickel in Nickel-Steel," by E. D. Campbell and W. H. Andrews: This Journal, 17, 127.

The presence of varying quantities of ammonium chloride in the nickel solution to be titrated has no effect on the titration. This is evident from the following :

| Taken. | | | Found. | | | | |
|---|---|---|---|---|---|---|---|
| $NH_4Cl$ present. | $Ni(NO_3)_2$. | Weight of Ni. | Readings. First. | Second. | Difference. | Blank. | Weight of Ni. |
| Grams. | cc. | Gram. | | | | | Gram. |
| 1 | 20 | 0.02 | 0.0 | 20.2 | 20.2 | 0.45 | 0.01996 |
| 3 | 20 | 0.02 | 20.2 | 40.5 | 20.3 | 0.45 | 0.02007 |
| 7 | 20 | 0.02 | 0.0 | 20.2 | 20.2 | 0.45 | 0.01996 |

1 cc. potassium cyanide solution = 0.001011 gram nickel.

Some of the results obtained by the foregoing method I append :

| Mark. | Solution of KCN equivalent to Ni. | Weight of nickel found. | Nickel. |
|---|---|---|---|
| | cc. | Gram. | Per cent. |
| 389 | 27.65 | 0.02795 | 1.397 |
| 389 | 27.65 | 0.02795 | 1.397 |
| 389 | 27.55 | 0.02785 | 1.392 |
| 390 | 28.60 | 0.02891 | 1.445 |
| 390 | 28.55 | 0.02886 | 1.443 |
| 382 | 30.40 | 0.03073 | 1.536 |
| 382 | 30.20 | 0.03053 | 1.527 |
| 387 | 31.00 | 0.03134 | 1.567 |
| 387 | 30.70 | 0.03104 | 1.552 |
| 387 | 31.00 | 0.03134 | 1.567 |
| 109 | 51.00 | 0.05156 | 2.578 |
| 109 | 51.30 | 0.05190 | 2.595 |

1 cc. potassium cyanide = 0.001011 gram nickel.

The above determinations were made on steels in which the manganese did not exceed one-tenth per cent. and in which there was no copper.

Different amounts of nickel were mixed with solutions containing two grams of iron and the nickel determined therein :

| Taken. | | Found. | |
|---|---|---|---|
| $Ni(NO_3)_2$ solution. | Weight of nickel. | KCN solution equivalent to Ni. | Weight of nickel. |
| cc. | Gram. | cc. | Gram. |
| 30 | 0.03 | 29.60 | 0.02992 |
| 30 | 0.03 | 29.05 | 0.02937 |
| 40 | 0.04 | 39.60 | 0.04003 |
| 40 | 0.04 | 39.70 | 0.0401 |
| 45 | 0.045 | 44.05 | 0.0445 |

For the estimation of nickel in ferronickel, dissolve twenty grams of the sample in aqua regia, evaporate to hard dryness take up with hydrochloric acid (1.1 sp. gr.), transfer to a liter flask, and dilute to the mark with water. Remove fifty cc., to which add five cc. strong hydrochloric acid, and concentrate to one-sixth its volume. Transfer to the separatory funnel, and proceed as with the steel.

A sample of ferronickel which, by an unknown method contained 33.93 per cent. of nickel, yielded 33.80, 34.00, 33.88, and 33.96 per cent. Another sample which, according to one chemist, contained 34.95 per cent. of nickel, gave 35.15 and 35.26 per cent.

The above-described method is, as can readily be seen, a combination of a modified portion of the method of Chase, with a slightly changed part of the procedure given by Campbell and Andrews. In the course pursued by Chase, two ether separations are necessary to remove the ferric chloride, while the separation, as worked by us, need not be repeated; but little ferric chloride is left, and the two ammonia precipitations are sufficient to completely remove the iron from the nickel.

With regard to the titration with potassium cyanide, that may be accomplished in the presence of most all the salts of ammonium and the mixed alkalies except the nitrates. The excess of ammonia should not in any case exceed three cc.[1]

While in steels, about which one knows nothing, it will be necessary to hunt for copper, yet in the general run of furnace work, copper is absent, and knowing such to be the case, the working with the unpleasant gas, hydrogen sulphide, is done away with entirely. As far as time is concerned, the method is short, requiring no longer time than the method of Chase.

In conclusion, I wish to here acknowledge the assistance of Mr. Clarence Ebaugh and Mr. John K. Faust in working out this method.

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[1] See "Estimation of Cyanogen," by Wm. J. Sharwood: This Journal, 19, 415.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 41.]

# THE QUANTITATIVE ESTIMATION OF BORIC ACID IN TOURMALINE.[1]

BY GEORGE W. SARGENT.

Received July 21, 1899.

## INTRODUCTION.

NOTHING of the constitution of this mineral is understood. In fact, exceedingly little is known concerning the structure of much less complex minerals. Structural formulas have been proposed, but these are conjectures only.

The problem that confronts the chemist undertaking to throw light upon the constitution of any of the products of nature's laboratory, is a very difficult one. No mode of attacking the problem has ever been devised. Substitutions, syntheses, and decompositions cannot be made as with organic bodies. There is no means of estimating the size of the molecule. The question of determining which elements are linked together in many instances seem unanswerable. Again, many elements are capable of existing in two conditions; this complicates the problem still further. Before attempting to answer these questions, however, the composition of the body must be known.

In a careful review of the literature of mineralogy, it will be noticed that in many cases some constituent of a mineral has been determined by difference, owing probably to the fact that no good direct method of estimating it existed at that time. Every chemist feels the necessity of directly determining any constituent. It is especially desirable that this be done in the analyses of complex substances. It may happen that many years have elapsed since the analysis of the mineral was made. Since then the old methods probably have been shown to be inaccurate, hence a redetermination is desirable. Owing to the difficulty of estimating boric acid, Rammelsberg, in numerous instances, in his analyses of tourmaline, obtained it by difference.

Boric acid constitutes from six per cent. to twelve per cent. of this mineral. Silica and alumina are its common associates from which it is separated with great difficulty. Since the time

[1] From the author's thesis presented for the Ph.D. degree, 1898.

of Rammelsberg, many methods have appeared, but few have been found applicable to insoluble borates or borosilicates; with tourmaline, they have proved tedious or unreliable. A chronological review of the various methods for the determination of this acid may be interesting. At least, it will show the condition in which the quantitative determination of boric acid rests at the present time.

## HISTORICAL RÉSUMÉ.

Probably the first work that was done toward the quantitative determination of boric acid, was that of Arfvedson.[1] By heating a mixture of borax and calcium fluoride with sulphuric acid, he volatilized the boron as fluoride; the sodium sulphate resulting from this treatment was dissolved out with water, evaporated to dryness, weighed, and the boric acid calculated.

Berzelius[2] attempted the determination by precipitating boron as potassium borofluoride. Berzelius also used Arfvedson's method with success, but in place of the calcium fluoride and sulphuric acid, he took hydrofluoric and sulphuric acids. In 1828, Menil[3] endeavored to estimate boric acid by means of the silver salt, $3Ag_2O.B_2O_3$, but met with little success. Gay Lussac,[4] in the year 1830, called attention to the titration of borax by a sulphuric acid solution with tincture of litmus as the indicator. The reaction is: $Na_2B_4O_7 + H_2SO_4 = Na_2SO_4 + 2B_2O_3$. The liquid changes color only when free sulphuric acid is present. This was the first volumetric method proposed.

Rose[5] was the first to volatilize boric acid as the ethyl ester and obtain its amount by difference. This was in 1850, but as early as 1732, Claude Geoffrey knew that boric acid imparted a characteristic green color to the alcohol flame and in 1818, Stromeyer[6] mentioned the volatility in an alcoholic solution and the characteristic green color given to the burning liquid. Rose, in his paper, gave a second method, in which a weighed amount of sodium carbonate was added to the borate, evaporated to dryness, and ignited until there was no further evolution of carbon

1 *K. Vetensk. Acad. Handb.*, (1822), 22, and *Schweigg. Jour.*, 8, 7.
2 *Lehrbuch*, 3, Aufl. 84; Pogg. *Ann.*, (1824), 2, 118.
3 *Jsb. d. Chem. und Phys.*, 2, 364.
4 *Ann. Chem. et Phys.*, 40, 398.
5 Pogg. *Ann.*, 80, 261.
6 *Ibid.*, 61, 179.

dioxide. The residue of sodium carbonate and boron trioxide was weighed and from this the boric acid calculated.

Berzelius' method gave poor results, owing to the solubility of the precipitate of potassium borofluoride in alcohol, with which it was washed to free it from potassium fluoride. Weber[1] tried modifying the method of Berzelius, in order to avoid the formation of the large quantity of fluoride, but did not succeed. Rammelsberg[2] found that if the alcohol used for washing the precipitate was free from water, potassium fluoride contaminated the precipitate, and that alcohol containing water dissolved some of the potassium borofluoride. Schweitzer[3] estimated the base and determined the boric acid by difference, by evaporating the base with hydrochloric acid until all the acid was expelled and estimating the chlorine as silver chloride.

In 1856, Kraut[4] showed that a borax solution boiled with ammonium chloride, reacted according to the following equation: $Na_2B_4O_7 + 2NH_4Cl = 2NaCl + 2B_2O_3 + 2NH_3$, and the ammonia could be caught in a standard acid solution, and thus the boric acid determined. This same year, the method of Stromeyer[5] appeared. He added to the solution of the borate two equivalents of potassium hydroxide to one equivalent of boron trioxide contained in the borate, then an excess of hydrofluoric acid and evaporated to dryness. The residue he dissolved in a twenty per cent. solution of potassium acetate, and filtered through a weighed filter, using a gutta percha funnel. The precipitate was washed first with a solution of potassium acetate to remove potassium fluoride, then with alcohol, dried at 100° C., and weighed. Upon applying this method to a silicate, Stromeyer obtained 97.5 per cent. of all the boron trioxide.

Where the boric acid content was approximately known, Schaffgotsch[6] added to the solution a weighed amount of sodium carbonate, in which not less than one and not more than two equivalents of sodium oxide ($Na_2O$) to two equivalents of boron trioxide were contained. After evaporation to dryness

1 Pogg. *Ann.*, **80**, 276 (1850).

2 *Ibid.*, **80**, 466 (1850).

3 *Pharm. Centrbl., Nr.* **24**, 390, and Fresenius' Anleitung zur quant. Analyse, 6 Aufl., (1875), **1**, 424.

4 *Henneberg's Jour. für Landwirtsch.*, **4**, 112; abs. by *Ztschr. anal. Chem.*, (1863), 73.

5 *Ann. Chem.* (Liebig), **100**, 82.

6 Pogg. *Ann.*, (1859), **107**, 427.

and ignition, the residue was sodium oxide and boron trioxide, the weight of which, less the weight of the sodium oxide taken, gave the boron trioxide. This method is essentially the same as that of Rose.

Marignac[1] in a solution containing alkali salts only, estimated the boric acid thus: After the addition of magnesium chloride, ammonium chloride, and ammonia, he evaporated the solution to dryness in a platinum dish. The residue after ignition was taken up with water and the insoluble portion removed: the filtrate was made ammoniacal, evaporated to dryness, ignited, the residue taken up with water, and the insoluble portion filtered off as before. This was repeated three times. The insoluble portions were ignited and weighed as magnesium pyroborate; the magnesia was determined by dissolving the pyroborate in nitric acid and precipitating as magnesium ammonium phosphate, and from this the boric acid was obtained by difference. Insoluble borates were fused with sodium carbonate, the melt extracted with water, and the solution acidified with hydrochloric acid; ammonia was then added and the whole concentrated to a small volume. Any precipitate that formed was filtered off; any lime present was removed as oxalate. The solution was then supposed to contain the borate together with alkali salts and was ready for the treatment with magnesium chloride solution. In regard to this method, Marignac himself says: "If good results are obtained, it is due to a balancing of errors."

Rose[2] substituted sodium metaborate for the sodium carbonate used in his earlier method. By fusing boric acid with calcium chloride in the presence of sodium and potassium chlorides, Ditte[3] obtained the salt $CaO,B_2O_3$ which crystallized from the fusion in needles and was insoluble in cold water. He utilized this salt for the estimation of the acid. In 1877, Berg[4] precipitated from an alcoholic solution $BaO,B_2O_3.4H_2O$. The precipitation was fairly completed, enabling him to determine boron trioxide in borax and obtain results within one tenth per cent. to three-tenths per cent. of the theoretical amounts.

1 *Ztschr. anal. Chem.*, (1862), **1**, 405.
2 Handb. der analyt. Chemie, 6 Aufl, **2**, 721 (1871).
3 *Compt. rend.*, **80**, 490 and 561 (1875).
4 *Ztschr. anal. Chem.*, **22**, 25.

Smith[1] precipitated manganese borate, $MnO.2B_2O_3$ from a borax solution in the presence of alcohol and determined the excess of manganous sulphate added, by evaporating the filtrate from the manganese borate to dryness, taking up with water and titrating the manganese according to Volhard.

In applying this method to a silicate, the latter was fused with sodium carbonate, the melt extracted with water and the solution digested with ammonium sulphate to throw out silica and alumina. After removing these, a known amount of manganous sulphate solution with an equal volume of alcohol was added; the precipitate was removed and the manganese in the filtrate determined as above. In a tourmaline, the percentage of boric acid found by Marignac's method was ten per cent., while that found by Smith's method was nine and seven-tenths per cent. Bodewig[2] tried the method of Smith upon a silicate, but obtained no result.

With some success, Bodewig used Stromeyer's method in the determination of the free acid, but upon applying it to a silicate, he experienced considerable difficulty in obtaining a solution of the borate free from silica. To accomplish this, the procedure of Berzelius (use of an ammoniacal zinc oxide solution) was resorted to with a fair degree of success.

The method of Gooch and Rosenbladt appeared simultaneously in 1887. Gooch[3] evaporated the solution of free boric acid to dryness with a weighed amount of lime and ignited to constant weight. The increase in weight represented boron trioxide. Rosenbladt[4] used magnesia in place of lime. Both Gooch and Rosenbladt showed that boric acid could be completely expelled from the concentrated acid solution of a borate as the methyl ester. To accomplish this, Gooch used an apparatus consisting of a large pipette bent at one end of the bulb at a right angle and at the other like a goose neck; the end of the pipette extended into a condenser. Insoluble borates were fused with sodium carbonate; the melt was extracted with water and the solution evaporated to dryness in the bulb of the pipette, which was immersed in a paraffin bath. The residue was made acid with nitric or acetic

1 *Am. Chem. J.*, (1882-83), **4**, 279.
2 *Ztschr. anal. Chem.*, **23**, 149 (1884).
3 *Am. Chem. J.*, **9**, 23.
4 *Ztschr. anal. Chem.*, **26**, 21.

acid and the distillation with methyl alcohol begun; the methyl alcohol was added in portions of ten cc. The distillate was poured into a platinum dish, containing a weighed amount of lime, evaporated to dryness and ignited to constant weight; the increase in weight represented boron trioxide.

The apparatus used by Rosenbladt was more simple than that used by Gooch. It consisted essentially of an Erlenmeyer flask connected with a condenser. Rosenbladt's method differed from Gooch's only in that the ester was caught in an ammonium carbonate solution, then poured into a dish containing a weighed amount of magnesia, and evaporated to dryness.

Morse and Burton,[1] to a concentrated borax solution of small volume, added sulphuric acid to acid reaction using tropaeoline OO as the indicator. After the addition of anhydrous copper sulphate, the resulting mass was extracted with absolute alcohol; this alcoholic solution was run into an excess of standard barium hydroxide. The excess of barium hydroxide was changed to carbonate, the whole evaporated to dryness and weighed as barium carbonate and barium metaborate, from which the boric acid was calculated. Insoluble borates were decomposed by fusion with sodium hydroxide in a nickel crucible. The extract of the fusion was evaporated to a small bulk and treated as the borax solution. By this procedure, Morse and Burton obtained from a tourmaline the following percentages of boron trioxide: 10.03 per cent., 10.08 per cent., and 10.11 per cent. Dr. Riggs obtained from the same tourmaline by a different method 10.15 per cent., 10.00 per cent., and 10.31 per cent. By means of a solution of baryta, Will[2] titrated boric acid.

Krüss and Moraht[3] in the analysis of beryllium borate, gave the method of Stromeyer preference. To the salt of the alkali metal, Parmentier[4] added an excess of hydrochloric acid or sulphuric acid. After dividing the solution into two equal parts, he added to one methyl orange and titrated the excess of hydrochloric or sulphuric acid; to the other, litmus was added and the total acidity determined. The difference gave the boric acid.

1 *Am. Chem. J.*, **10**, 154 (1888).
2 *Arch. d. Pharm.*, **225**, 1101; abs. by *Ztschr. anal. Chem.*, **28**, 100 (1889).
3 *Ann. Chem.* (Liebig), **259**, 184 (1890).
4 *Compt. rend.*, **113**, 41 (1891).

Reischle[1] stated, that the color reaction of the litmus was so indistinct that he could obtain no results.

In 1893, Thompson[2] noticed that a boric acid solution containing thirty per cent. of glycerol could be titrated with sodium hydroxide with phenolphthalein as the indicator. Starch, glucose, and cane-sugar could be substituted for glycerol. In borax the acid was set free by hydrochloric acid using methyl orange as the indicator and the boric acid titrated by a solution of sodium hydroxide with glycerol and phenolphthalein. Thompson applied this method to boracite.

As the commercial method of estimating boron trioxide in boronatrocalcites, Le Roy[3] gave the following: Decompose the mineral with dilute sulphuric acid and hydrochloric acid in a flask connected with a reflux condenser; remove the insoluble residue and precipitate the iron and aluminum as hydroxides by caustic soda. After the removal of these, the solution is made acid with hydrochloric acid and boiled to expel carbon dioxide; upon cooling, it is made up to a known volume. Twenty cc. of this solution are titrated with standard alkali and Porrier orange III, until the shade produced corresponds to the yellowish red caused by the same amount of orange III in twenty cc. of water. Another volume of twenty cc. is now titrated with alkali using orange II as the indicator, until the color is a dark red. The difference between the two titrations indicates the boric acid present.

Schwarz[4] suggested Congo red as an indicator to be used with hydrochloric acid. Hefelmann[5] gave litmus the preference. Hefelmann recommends the expulsion of the boric acid by heating with ammonium fluoride and the estimation of it by difference.

Barthe[6] used the method of Thompson with success as did also Hönig and Spitz.[7] Insoluble silicates were fused by the latter with sodium and potassium carbonates. The melt was dissolved in water and as much ammonium chloride added as equaled the carbonates used in the fusion. The solution was then boiled

1 *Ztschr. anorg. Chem.*, **4**, 111 (1893).
2 *J. Soc. Chem. Ind.*, **12**, 432.
3 *Ibid.* (1893), 867.
4 *Pharm. Zig.*, **32**, 562 (1894).
5 *Pharm. Centralhalle* (N. F.), 1894, **9**, 116.
6 *J. Pharm. Chem.*, **29**, 163 (1894).
7 *Ztschr. angew. Chem.*, (1896), 550.

and the precipitated silica removed. The last traces of silica were removed by Berzelius' method. After concentration to a small volume, the liquid was made acid with hydrochloric acid, boiled a few minutes to expel carbon dioxide and titrated. By this procedure, the percentage of boron trioxide found in a "Gasglühlicht-cylinder" was 5.12 per cent., while that found by difference was 5.34 per cent.

Hönig and Spitz also applied the reaction made use of by Kraut ($Na_2B_4O_7 + 2NH_4Cl = 2NH_3 + 2NaCl + 2B_2O_3$) to "Borax-kalk." The results obtained differed 0.10 per cent. to 0.30 per cent. from those gotten by their first method. In 1897, Kraut[1] employed Gooch's method successfully for the analysis of colemanite and pandermite. The apparatus used in the distillation of the ester was, however, more simple than that of Gooch. Schneider and Gaab[2] distilled the boric acid with alcohol and evaporated the distillate with a weighed amount of sodium carbonate.

By shaking with ether, Bellocq[3] removed boric acid from other salts, and upon the evaporation of the ethereal extract obtained the trioxide.

Thaddeeff[4] applied the Berzelius-Stromeyer method, somewhat modified, to borax. His modification consisted in adding to the potassium acetate solution containing the potassium borofluoride, 100 cc. of alcohol, 0.805 sp. gr., and allowing it to stand twelve to fourteen hours before filtering. The precipitate was washed with alcohol of the same specific gravity. By this means, results varying from 0.08 per cent. to 0.40 per cent. of the theoretical were obtained. Thaddeeff also volatilized boric acid as the methyl ester which was caught in a solution of potassium hydroxide. From this potassium borofluoride was precipitated. To facilitate the volatilization of the ester, Thaddeeff used a current of air. By this procedure, he obtained results varying from 0.01 per cent. to 0.40 per cent. of the theoretical.

## INVESTIGATION.

From this review, it is apparent that, while boric acid in borax, soluble borates, and minerals not requiring fusion with alkalies

1 *Ztschr. anal. Chem.*, **36**, 165.
2 *Pharm. Centralhalle*, **37**, 672 (1897).
3 *Rev. Int. falsific.* **9**, 119; abs. by *Ztschr. anorg. Chem.*, 380 (1897).
4 *Ztschr. anal. Chem.* **36**, 568 (1897).

for their decomposition, is estimated with a fair degree of success, this acid, where fusion is required, is not determined with the desired accuracy. Minerals containing silica and alumina usually require fusion with sodium carbonate or caustic soda for their decomposition. The extract from this fusion is supposed to contain all the boric acid together with silicate and aluminate of soda. Digestion with ammonium chloride or sulphate is generally resorted to for the removal of the latter two. The solution is then ready for treatment according to any method applicable to borax.

The methods of Gooch, Stromeyer, and Marignac have been universally used. If Marignac's method is adopted, results are obtained about which there is more or less uncertainty. If Stromeyer's method is used, the potassium borofluoride weighs more than it should, owing to fluosilicate.[1] To avoid this silica, Wöhler[2] recommends evaporating the hydrochloric acid solution of the fusion to dryness, in a flask connected with a condenser, adding the distillate to the residue and filtering off the silica. By this means, silica is entirely removed, but alumina and other bases are yet to be separated, and in the removal of the alumina as hydroxide, there is a tendency on the part of the precipitate to retain boric acid.[3] In the use of Gooch's method the trouble is met in weighing the lime.

It is evident from the foregoing, that the quantitative determination of this acid, where it exists in such combination as it does in tourmaline, is not attended with the most desirable results. With the hope of obtaining a more accurate and more rapid method and of casting some light, perhaps, upon the constitution of this mineral, this investigation was undertaken.

The isolation of the acid is evidently necessary for its successful determination. Its separation from these two associates, silica and alumina, is difficult, and alkalies apparently increase this difficulty; hence it was thought, if the tourmaline could be decomposed by heating with metallic magnesium or fusion with carbonates other than those of the alkalies, the isolation of the boric acid would be more readily accomplished; or if the tourmaline was fused with alkali carbonates, possibly it could be

1 Fresenius' Quant. Chem. Anal., 424.
2 (*Handb. der Mineral Analyse*, under Datholite.)
3 Wöhler: *Ann. Chem. Pharm.*, 141, 268.

completely removed from these objectionable associates in an acid solution.

Since the volumetric method of Thompson seemed to offer the most rapid and accurate means, I decided to investigate it, with the view of utilizing it for the determination of the isolated boric acid.

### DETERMINATION OF BORIC ACID IN BORAX BY THE METHOD OF THOMPSON.

One-tenth normal hydrochloric acid solution was prepared and standardized by precipitating the chlorine with silver nitrate.

I. Ten cc. hydrochloric acid solution gave 0.1430 gram silver chloride = 0.035358 gram chlorine.

II. Ten cc. hydrochloric acid solution gave 0.1440 gram silver chloride = 0.035605 gram chlorine.

| | Chlorine. Gram. |
|---|---|
| Average | 0.035481 |
| Theory | 0.03545 |
| Difference | 0.000031 |

For this hydrochloric acid solution a tenth-normal caustic soda solution was prepared. A borax solution, ten cc. of which contained one gram of $Na_2B_4O_7.10H_2O$, or 0.03659 gram of $B_2O_3$, was prepared from recrystallized borax. As nearly all glycerol is likely to be acid owing to fatty acids, it was found best to add a very small amount of water to the glycerol, then phenolphthalein, shake well, and introduce sodium hydroxide until a faint pink tinge appeared. This neutralized glycerol was kept in a well-stoppered bottle.

For the estimation of boric acid in the latter, a number of cubic centimeters of the borax solution were introduced into an Erlenmeyer flask, a few drops of methyl orange added and tenth-normal hydrochloric acid run in from a burette until all the boric acid was free; fifty cc. of the glycerol were added, together with a few drops of phenolphthalein, and the titration with tenth-normal caustic soda begun. According to the reaction $2B_2O_3 + 4NaOH = 4NaBO_2 + 2H_2O$, one cc. of tenth-normal alkali is equivalent to 0.0035 gram of boron trioxide.

The following table shows the value of this method :

| Taken. | | | Found. | | |
|---|---|---|---|---|---|
| | Borax solution O. | $B_2O_3$. | $\frac{N}{10}$ NaOH. | $B_2O_3$. | |
| No. | cc. | Gram. | cc. | Gram. | Per cent. |
| 1 | 10 | 0.03659 | 10.4 | 0.0364 | 36.40 |
| 2 | 10 | 0.03659 | 10.5 | 0.03675 | 36.75 |
| 3 | 10 | 0.03659 | 10.4 | 0.3640 | 36.40 |
| 4 | 20 | 0.07318 | 21.0 | 0.0735 | 36.75 |
| 5 | 20 | 0.07318 | 20.9 | 0.07315 | 36.57 |
| 6 | 25 | 0.09147 | 26.1 | 0.09135 | 36.54 |
| 7 | 25 | 0.09147 | 26.1 | 0.09135 | 36.54 |
| 8 | 15 | 0.05488 | 15.7 | 0.05495 | 36.63 |
| 9 | 15 | 0.05488 | 15.7 | 0.05495 | 36.63 |
| 10 | 15 | 0.05488 | 15.6 | 0.0546 | 36.40 |

The atomic weights used were:

Oxygen = 16.00 Boron = 10.95
Silver = 107.97 Chlorine = 35.45
Sodium = 23.05

The theoretical percentages of the constituents of crystallized borax are:

| | Per cent. |
|---|---|
| Sodium oxide | 16.26 |
| Boron trioxide | 36.59 |
| Water | 47.15 |

Having proved the volumetric method of Thompson to give reliable results with borax, the problem of isolating the boric acid in tourmaline was taken up.

### DECOMPOSITION OF TOURMALINE BY HEATING WITH METALLIC MAGNESIUM.

Two-tenths of a gram of brown tourmaline (No. 2) were heated to expel the water, mixed with half a gram of magnesium powder, the whole placed in a porcelain crucible and covered with a thick layer of thoroughly dried salt. It was then heated for thirty minutes and allowed to cool. The contents, which had the appearance of amorphous silicon, together with any parts of the crucible to which the contents adhered, were powdered, placed in a porcelain boat, and chlorine passed over the same. The chlorine and any volatile portion were caught in two U-tubes containing water; later, heat was applied and gradually raised to a dull red, where it was held until the contents of the boat became quiescent. The heat was then gradually withdrawn.

After four days, most of the chlorine had gone from the U-tubes, leaving the contents exceedingly acid. Sodium carbonate sufficient to neutralize the acid was added, and the solution evaporated almost to dryness. After making acid and expelling the carbon dioxide by drawing air through the solution for fifteen minutes, the excess of acid was neutralized by sodium hydroxide with methyl orange as the indicator, and the boric acid titrated with the following results:

| No. | Weight of mineral. Gram. | $\frac{N}{10}$ NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|---|
| 1 | 0.2000 | 5.0 | 0.0175 | 8.75 |
| 2 | 0.2000 | 2.5 | 0.00875 | 4.357 |
| 3 | 0.2000 | 1.2 | 0.0042 | 2.10 |
| 4 | 0.2000 | 2.0 | 0.007 | 3.50 |
| 5 | 0.2000 | 1.5 | 0.00525 | 2.625 |

No. 4 was allowed to stand two days before treating the contents of the U-tubes. Very little acid was present. Nos. 2, 3, and 5 were allowed to stand but a few hours before treating. Little acid was present and the chlorine was removed in each instance before the addition of the sodium carbonate, by drawing air through the tubes. It might be added, that the time of heating the mineral with the magnesium powder was varied from fifteen minutes to an hour, and in every case the contents of the crucible had the appearance of amorphous silicon.

This procedure is evidently not a success; just why, I do not know, but am inclined to believe that the boron chloride was not completely broken up when it came in contact with the water saturated with chlorine, but was carried on out with the escaping gas. It may have been that the mineral was not completely decomposed by the magnesium, but from all appearances the magnesium had entirely reduced it. At any rate, this procedure was abandoned, and the fusion of the mineral with the alkaline earth carbonates undertaken.

### DECOMPOSITION OF TOURMALINE BY FUSION WITH CALCIUM CARBONATE.

Some of the very finely powdered mineral was fused with a mixture of eight times its weight of precipitated calcium carbonate and its own weight of ammonium chloride, at a low red heat for one hour, as in the J. Lawrence Smith fusion for

the alkalies; when cool the fusion was powdered, placed in a platinum dish, covered with water, and an amount of sodium carbonate introduced slightly in excess of that required. After digesting for half an hour the solution was allowed to cool and the insoluble portion was removed. To the filtrate sulphuric acid to almost neutral reaction was added. The precipitate which formed was filtered off and the solution made slightly acid. For fifteen minutes air was drawn through the solution to remove the carbon dioxide, after which the excess of acid was neutralized with caustic soda, with methyl orange as the indicator, and the boric acid titrated.

In this instance half-normal sodium hydroxide was used in the titration of the boric acid. One cc. of a half-normal alkali solution is equivalent to 0.0175 gram of boron trioxide. The results are shown in this table:

| No. | Weight of mineral. Gram. | $\frac{N}{2}$ NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|---|
| 1 | 0.3000 | 2.4 | 0.0420 | 14.00 |
| 2 | 0.3000 | 2.8 | 0.0490 | 16.33 |
| 3 | 0.3000 | 3.7 | 0.06475 | 21.58 |

The decomposition of the mineral was complete, because all the portion insoluble in water, except silica, dissolved in hydrochloric acid. Upon allowing the titrated solutions to stand, in every case a precipitate of alumina separated. Thinking that during the boiling of the fusion with soda some alumina was dissolved, I used barium carbonate in the place of the soda and decomposed the fusion by boiling with sodium sulphate, with the hope of avoiding the solution of alumina.

That this was not a success is shown by the following:

| No. | Weight of mineral (No. 2). Gram. | $\frac{N}{2}$ NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|---|
| 1 | 0.3000 | 1.5 | 0.02625 | 8.75 |
| 2 | 0.3000 | 3.3 | 0.05775 | 19.25 |
| 3 | 0.3000 | 4.3 | 0.07525 | 25.08 |
| 4 | 0.3000 | 2.6 | 0.0455 | 15.16 |
| 5 | 0.3000 | 2.1 | 0.03675 | 12.25 |
| 6 | 0.3000 | 1.85 | 0.3237 | 10.79 |

In every instance, after titration, a copious precipitate of alumina came down upon boiling with hydrochloric acid and adding an excess of ammonia. It is very likely that in the

digestion of the fusion with sodium sulphate, barium carbonate becomes barium sulphate and sodium carbonate is formed; this then dissolves the alumina.

I thought that possibly this alumina might be eliminated completely by adding a small quantity of ammonium sulphate to the sodium sulphate solution free from the insoluble portion, and digesting with a reflux condenser; the ammonia could easily be expelled by boiling with an excess of alkali. This was done and the following results obtained:

| No. | Weight of mineral (No. 2). Gram. | $\frac{N}{2}$NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|---|
| 1 | 0.5000 | 2.6 | 0.0455 | 9.10 |
| 2 | 0.5000 | 2.25 | 0.03937 | 7.87 |
| 3 | 0.5000 | 2.00 | 0.0350 | 7.00 |

Upon testing after the titration, alumina was found. The insoluble portions of some of these fusions were fused with sodium carbonate, and the boric acid therein, determined by distillation with methyl alcohol—a method which will be given later—and the following amounts found:

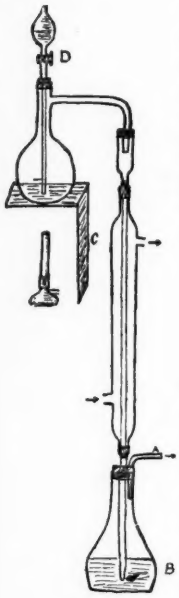
| No. | Weight of mineral (No. 2). Gram. | $\frac{N}{2}$NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|---|
| 2 | 0.3000 | 1.1 | 0.01925 | 6.41 |
| 3 | 0.3000 | 0.6 | 0.0105 | 3.50 |
| 1 | 0.5000 | 1.0 | 0.0175 | 3.50 |
| 2 | 0.5000 | 1.1 | 0.01925 | 3.85 |
| 3 | 0.5000 | 1.4 | 0.0245 | 4.90 |

From this it appears that the decomposition of tourmaline by fusing the mineral with calcium or barium carbonate, is not a success; nor is it a success with datolite, as the following show:

| No. | Weight of mineral. Gram. | $\frac{N}{2}$NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|---|
| 1 | 0.5000 | 4.6 | 0.0805 | 16.10 |
| 2 | 0.3000 | 2.8 | 0.0490 | 16.33 |

The decompositions were complete, but some boric acid had remained with the insoluble portions.

Tourmaline to be completely decomposed must be fused with alkalies. Then if boric acid is to be cleanly removed from the alumina, it must be done in an acid solution. The methods of Gooch and Rosenbladt are the only means of accomplishing this




and directly estimating the boric acid; but the process as practiced by Gooch or Rosenbladt is rather slow. Thaddeeff lessened the time necessary for the complete removal of the boric acid as the methyl ester, by using a current of air. By utilizing the discovery of Gooch and Rosenbladt and the volumetric method of Thompson, I thought a rapid and accurate method could be devised.

### THE VOLATILIZATION OF THE BORIC ACID AS THE METHYL ESTER AND SUBSEQUENT TITRATION.

To diminish the time required for the complete volatilization, an apparatus, the plan of which is here shown, was constructed. A weighed amount of fused borax was placed in the bulb, moistened with sulphuric acid, ten cc. of commercial wood alcohol added, and the distillation begun. The distillate was caught in the flask B, which contained twenty-five cc. of tenth-normal caustic soda, into which the condenser tube extended about one inch. When nearly all the alcohol had distilled over, air was drawn through the whole apparatus for a few minutes, by attaching a suction-pump to A and opening the stopcock at D sufficiently far to let the air gently bubble through the solution in B. This operation was repeated until fifty cc. of wood alcohol had been added and distilled off into the sodium hydroxide. The flask was disconnected; twenty-five cc. of tenth-normal hydrochloric acid were introduced, then 100 cc. of glycerol with a few drops of phenolphthalein and the titration of the boric acid with tenth-normal alkali begun. By this procedure the following results were obtained:

| | Taken. | | Found. | | |
|---|---|---|---|---|---|
| | Weight of borax. | $B_2O_3$. | $\frac{N}{10}$ NaOH. | $B_2O_3$. | |
| No. | Gram. | Gram. | cc. | Gram. | Per cent. |
| 1 | 0.1000 | 0.06924 | 23.00 | 0.0805 | 80.50 |
| 2 | 0.1000 | 0.06924 | 22.80 | 0.0794 | 79.80 |

The theoretical percentages of the constituents of fused borax are:

| | Per cent. |
|---|---|
| Sodium oxide | 30.76 |
| Boron trioxide | 69.24 |

The amount of alcohol in each case being the same and the results obtained agreeing so closely, I concluded that the alcohol was the cause of the high percentages. Upon evaporating the distillate obtained as above and igniting, a black charred mass was left, which, however, was easily burned. This showed either that some organic compound had been formed in the distillation of the alcohol from the sulphuric acid or existed as an impurity in the alcohol and was carried over during the distillation. If the substance were acetic acid or formic acid, the sodium salt would be formed, which when treated with hydrochloric acid would regenerate the acid and thus increase the amount of sodium hydroxide required.

To ascertain whether a formate was produced, some pure methyl alcohol was distilled with sulphuric acid. The distillate which was caught in caustic soda, was concentrated, the alkali neutralized with nitric acid and silver nitrate added. The odor of formic acid was distinctly preceptible upon neutralizing the sodium hydroxide, and upon adding the silver nitrate and boiling, silver separated. When the ester comes in contact with the alkali, the probable reaction is: $B(OCH_3)_3 + NaOH + H_2O = BOONa + CH_3OH$. The heating of methyl alcohol with sulphuric acid in the air seems to react thus: $CH_3OH + O_2 = H_2O + HCOOH$.

To destroy this organic acid, the distillate was evaporated to a small volume, carbon dioxide rapidly run through to insure the formation of borax, the evaporation then continued to dryness and the residue ignited until all the carbon was consumed. When cool, hydrochloric acid was added in slight excess and the carbon dioxide removed by drawing air through the solution for a quarter of an hour. The excess of hydrochloric acid was neutralized and the boric acid titrated with half-normal sodium hydroxide.

| | Taken. | | Found. | | |
|---|---|---|---|---|---|
| | Weight of borax. | $B_2O_3$. | $\frac{N}{10}$ NaOH. | $B_2O_3$. | |
| No. | Gram. | Gram. | cc. | Gram. | Per cent. |
| 1 | 0.2000 | 0.13848 | 9.0 | 0.1575 | 78.75 |
| 2 | 0.2000 | 0.13848 | 8.2 | 0.1435 | 71.75 |
| 3 | 0.1000 | 0.06924 | 4.0 | 0.0700 | 70.00 |

These results are too high and variable, so pure methyl alcohol was substituted for the commercial article and about sixty cc. were used each time. The boric acid was titrated in this instance with tenth-normal caustic soda. It will be noticed that sometimes tenth-normal alkali was used in the titration, and at other times half-normal. Either gave good results in the titration of boric acid in borax, but with half-normal sodium hydroxide, the end-reaction was more pronounced.

| | Taken. | | Found. | | |
|---|---|---|---|---|---|
| | Weight of borax. | $B_2O_3$. | $\frac{N}{10}$NaOH. | $B_2O_3$. | |
| No. | Gram | Gram. | cc. | Gram. | Per cent. |
| 1 | 0.5000 | 0.3462 | 97.5 | 0.34125 | 68.25 |
| 2 | 0.2000 | 0.13848 | 39.5 | 0.13825 | 69.13 |
| 3 | 0.3000 | 0.20772 | 58.8 | 0.2058 | 68.60 |

According to these reactions: $4B(OH)_3+4NaOH=4BO.ONa+8H_2O$ and $4BO.OH+4NaOH=4BO.ONa+2H_2O$, the treatment with carbon dioxide was unnecessary and was dispensed with in the following determinations:

| | Taken. | | Found. | | |
|---|---|---|---|---|---|
| | Weight of borax. | $B_2O_3$. | $\frac{N}{10}$NaOH. | $B_2O_3$. | |
| No. | Gram. | Gram. | cc. | Gram. | Per cent. |
| 1 | 0.2000 | 0.13848 | 39.8 | 0.1393 | 69.65 |
| 2 | 0.3000 | 0.20772 | 59.4 | 0.2079 | 69.30 |
| 3 | 0.4000 | 0.27696 | 79.3 | 0.2775 | 69.36 |
| 4 | 0.2000 | 0.13848 | 39.6 | 0.1386 | 69.30 |

The theoretical per cent. of acid in fused borax is 69.24. This shows that this method is a good one, applied to borax. The next thing was to apply it to tourmaline.

A brown tourmaline, marked (No. 2), from McAffee, New Jersey, on analysis gave the following:

| | Per cent. |
|---|---|
| Silica | 33.72 |
| Boric acid | 10.00 |
| Alumina | 25.88 |
| Ferric oxide | 1.82 |
| Ferrous oxide | 3.23 |
| Lime | 6.92 |
| Magnesia | 14.07 |
| Loss on ignition | 1.80 |
| Potassium oxide | 0.20 |
| Sodium oxide | 2.52 |

In this instance, the boric acid was estimated according to

Marignac's method. The tourmaline was fused with potassium and sodium carbonates; the fusion was taken up with water, evaporated almost to dryness, then transferred to the distilling bulb together with the insoluble oxides. The distilling bulb instead of resting on an asbestos pad, was immersed to half the depth of the bulb, in a glycerine bath. The temperature of the bath was raised to 135° C. and the contents of the flask rapidly evaporated to dryness by the aid of a current of air. This required about an hour. The glycerine bath was allowed to cool down to 50° C. and a flask containing sodium hydroxide was substituted for the one previously used to catch the distillate. The contents of the bulb were made decidedly acid and the distillation with methyl alcohol commenced. The remainder of the operation was the same as with borax.

The following table shows the results of this method:

| | Weight of mineral (No. 2). | $\frac{N}{10}$NaOH. | $B_2O_3$. | |
|---|---|---|---|---|
| No. | Gram. | cc. | Gram. | Per cent. |
| 1 | 0.5000 | 16.0 | 0.0560 | (11.20) |
| 2 | 0.5000 | 16.0 | 0.0560 | (11.20) |
| 3 | 1.0000 | 31.0 | 0.1085 | (10.85) |
| 4 | 1.0000 | 22.4 | 0.0784 | (7.84) |
| 5 | 1.0000 | 27.4 | 0.0959 | 9.59 |
| 6 | 0.5000 | 13.6 | 0.0476 | 9.52 |
| 7 | 0.5000 | 13.7 | 0.04795 | 9.59 |

In Nos. 5, 6 and 7, the fusion was allowed to cool completely and by rolling the crucible between the fingers with gentle pressure, the fusion dropped out. It was placed in the distilling flask, the crucible rinsed with sulphuric acid (1 : 1), and the washings added. Sulphuric acid and water sufficient to break the mass up into a mushy state, were poured over it and the distillation with methyl alcohol conducted as with the others. By the procedure used in these latter determinations, the entire time consumed was about five hours.

A black tourmaline which gave, according to Marignac's method, 9.87 per cent. of boric acid, treated by the above method gave the following:

| | Weight of mineral. | $\frac{N}{2}$NaOH. | $B_2O_3$. | |
|---|---|---|---|---|
| No. | Gram. | cc. | Gram. | Per cent. |
| 1 | 0.5000 | 2.9 | 0.05075 | 10.15 |
| 2 | 0.5000 | 2.9 | 0.05075 | 10.15 |

From datolite, the following percentages were obtained:

| No. | Weight of mineral. Gram. | $\frac{N}{2}$NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|---|
| 1 | 0.5000 | 5.50 | 0.09625 | 19.25 |
| 2 | 0.5000 | 5.55 | 0.097125 | 19.43 |

Another sample of a brown tourmaline marked No. 4 gave these results:

| No. | Weight of material. Gram. | $\frac{N}{2}$NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|---|
| 1 | 0.5000 | 2.80 | 0.0490 | 9.80 |
| 2 | 0.5000 | 2.90 | 0.05075 | 10.15 |
| 3 | 0.5000 | 2.85 | 0.04988 | 9.976 |
| 4 | 1.0000 | 5.70 | 0.09975 | 9.975 |

In each of the preceding determinations the residue in the distilling bulb was tested for boric acid, but none was found. These results show this to be a good method of estimating boric acid wherever it is associated with silica and alumina. The time consumed is considerably less than that required by other methods, and the complete isolation of the boric acid is accomplished. The construction of the apparatus required by this method is an objection, a very slight one, however.

It occurred to me that possibly a more simple method might be found in that proposed by Smith.[1] With this in view I took up the method of Smith for investigation.

## ESTIMATION OF BORIC ACID BY THE METHOD OF SMITH.

A borax solution, one cc. of which contained 0.004 gram of $Na_2B_4O_7$, a potassium permanganate solution containing zinc sulphate, one cc. of which was equivalent to 0 0018705 gram of manganese, and a manganous sulphate solution containing 0.005228 gram of manganese in each cubic centimeter, were prepared. To a volume of the manganous sulphate solution, a known portion of the borax solution, with an equal quantity of alcohol, was added. As soon as the precipitate settled it was filtered off by means of a Gooch crucible and a suction-pump. The filtrate containing the excess of manganous sulphate was evaporated to dryness, the residue gently ignited and when cool dissolved in water. A few drops of a saturated solution of sulphur dioxide were added to aid in dissolving the residue.

[1] *Am. Chem. J.*, 4, 279.

The liquid was then transferred to a flask and brought to boiling. The titration of the manganese according to Volhard's method was now made, and from this the boric acid calculated by the reaction $MnSO_4 + Na_2B_4O_7 = MnB_4O_7 + Na_2SO_4$.

| No. | Borax solution. cc. | Borax. Gram. | $MnSO_4$ solution. cc. | Manganese. Gram. | $KMnO_4$. cc. | Excess of Mn. | $B_2O_3$. Per cent. | Volume alcohol. |
|---|---|---|---|---|---|---|---|---|
| 1 | 10 | 0.04 | 5 | 0.02614 | 8.0 | 0.014964 | 71.03 | 15 |
| 2 | 10 | 0.04 | 5 | 0.02614 | 8.0 | 0.014964 | 71.03 | 15 |
| 3 | 10 | 0.04 | 5 | 0.02614 | 8.2 | 0.015338 | 68.33 | 10 |
| 4 | 10 | 0.04 | 10 | 0.05228 | 22.1 | 0.041338 | 68.91 | 10 |
| 5 | 15 | 0.06 | 10 | 0.05228 | 18.9 | 0.035354 | 71.71 | 15 |
| 6 | 15 | 0.06 | 10 | 0.05228 | 19.2 | 0.035914 | 69.38 | 15 |
| 7 | 25 | 0.10 | 15 | 0.07842 | 27.3 | 0.051065 | 69.54 | 20 |
| 8 | 25 | 0.10 | 15 | 0.07842 | 27.3 | 0.051065 | 69.54 | 20 |
| 9 | 25 | 0.10 | 25 | 0.13071 | 55.3 | 0.10344 | 69.30 | 25 |
| 10 | 20 | 0.08 | 20 | 0.10456 | 43.5 | ..... | (67.68) | 20 |

The precipitate of $MnO.2B_2O_3$ was dissolved off the filter by a warm aqueous solution of sulphur dioxide, transferred to a flask, brought to boiling, and the manganese then titrated with potassium permanganate according to the method of Volhard. This was done with each precipitate with the following results:

| No. | $KMnO_4$. cc. | Gram Mn with $2B_2O_3$. | $B_2O_3$. Per cent. | Total Mn determined. | Difference from amount taken. |
|---|---|---|---|---|---|
| 1 | 6.0 | 0.011223 | 71.31 | 0.026187 | 0.000046 plus. |
| 2 | 6.0 | 0.011223 | 71.31 | 0.026187 | 0.000046 plus. |
| 3 | 5.8 | 0.010849 | 68.94 | 0.026187 | 0.000046 plus. |
| 4 | 5.9 | 0.011036 | 70.11 | 0.052374 | 0.000052 plus. |
| 5 | 9.0 | 0.016834 | 71.31 | 0.052188 | 0.000094 minus. |
| 6 | 9.0 | 0.016834 | 71.31 | 0.052188 | 0.000466 plus. |
| 7 | 14.5 | 0.027122 | 68.94 | 0.078187 | 0.000236 minus. |
| 8 | 14.7 | 0.027496 | 69.89 | 0.078561 | 0.000138 plus. |
| 9 | 14.6 | 0.027310 | 69.41 | 0.130750 | 0.000045 plus. |
| 10 | 15.0 | 0.028057 | 71.31 | ..... | ..... |

This shows that boric acid in borax may be successfully estimated either by the titration of the excess of manganous sulphate, which is Smith's method, or by titration of the manganese combined with boron trioxide.

For the estimation of boric acid in a tourmaline, Smith digested the extract of the sodium carbonate fusion with an amount of ammonium sulphate equivalent to the carbonate. The precipitate that formed was removed and the filtrate concentrated to twenty-five cc., after which it was treated as the borax

solution. This I did, but upon adding the manganous sulphate obtained no precipitate, and upon testing with litmus, found the liquid acid. This corroborates Bodewig's statement.[1] Another fusion was made and the extract evaporated to a volume of twenty cc., then transferred to a flask connected with a reflux condenser, and digested with ammonium sulphate. The precipitate was removed and the filtrate and washings concentrated to a volume of twenty-five cc. To the solution, which was faintly ammoniacal, a known volume of manganese sulphate, with an equal volume of alcohol, was added. As soon as the precipitate had settled it was filtered off and washed with alcohol and water (one to one). The filtrate was evaporated to dryness and the residue ignited; when cool, it was taken up with water and a drop of aqueous sulphur dioxide added. The liquid was brought to boiling and the manganese titrated with potassium permanganate. Two determinations gave respectively 23 per cent. and 28.12 per cent. of boric acid.

There is no doubt but that in the ammoniacal solution manganic hydroxide is formed and carried down with the manganese borate. I dissolved this precipitate in aqueous sulphur dioxide, and attempted to remove the manganese from the boron trioxide, in order to titrate the boron trioxide with sodium hydroxide, but could find no means of separating the two without volatilizing some boric acid or introducing harmful reagents.

My attention was next turned towards the method used by Hönig and Spitz[2], for the determination of boric acid in a "Gasglühlichtcylinder," with the hope of obtaining a simple method applicable to tourmaline.

### THE HÖNIG AND SPITZ METHOD OF DETERMINING BORIC ACID IN INSOLUBLE SILICATES.

The extract of the fusion of a brown tourmaline was digested with an amount of ammonium chloride, equivalent to the carbonate used in the fusion, and the precipitated alumina and silica filtered off. An ammoniacal zinc oxide solution was added, and the whole boiled until all the ammonia was expelled. The zinc oxide, with any silica it carried, was removed and the filtrate concentrated to a small volume. After being made

[1] *Ztschr. anal. Chem.*, **23**, 143.
[2] *Ztschr. angew. Chem.* (1896), 551.

slightly acid with hydrochloric acid, the solution was boiled for fifteen minutes in a flask connected with a reflux condenser; when cooled the condenser was washed out with water (the washings going into the flask), and after neutralizing the excess of hydrochloric acid, the titration for boric acid was made. The results obtained were very high, and in every instance after titration, a white precipitate which proved to be alumina and zinc oxide, separated. This further shows that boric acid cannot be separated from alumina by digestion with ammonium salts and that the removal of zinc oxide by this means is a difficult task. The following course was then pursued. After the addition of ammonium chloride, the extract of the fusion was evaporated to dryness, the residue gently ignited to expel the ammonium chloride and when cool taken up with water. Any insoluble matter was removed, a small amount of sodium carbonate added and the whole boiled for a few minutes. When cool, the carbon dioxide was expelled by adding hydrochloric acid and boiling, and the boric acid titrated after neutralizing the excess of hydrochloric acid. Tenth-normal sodium hydroxide was used with the following results:

| | Weight of mineral (No. 2). | $\frac{N}{10}$ NaOH. | $B_2O_3$. | |
|---|---|---|---|---|
| No. | Gram. | cc. | Gram. | Per cent. |
| 1 | 0.2000 | 4.5 | 0.01575 | 7.875 |
| 2 | 0.5000 | 10.5 | 0.03675 | 7.35 |
| 3 | 0.5000 | 11.2 | 0.0392 | 7.84 |

These results are lower than those previously obtained in the same sample (page 875), and are due to the volatilization of some of the boric acid during the ignition necessary to completely expel the ammonium salts, and it may be that some of the acid is lost in the boiling with the ammonium salt. In commenting on the method of Smith, Bodewig[1] says that some of the boric acid resulting from the decomposition of the borax by the ammonium salt, would be volatilized in the boiling; upon testing the escaping vapor, he found it alkaline, while the solution at the same time was acid.

To determine just how much boric acid was volatilized in this way, I decomposed a solution 200 cc. in volume, containing one gram of $Na_2B_4O_7$, by distilling with ammonium chloride; the

[1] *Ztschr. anal. Chem.* (1884), 143.

solution was distilled to one-fourth its volume. The distillate contained 0.02275 gram of boron trioxide, equivalent to 2.275 per cent. of the borax or 3.29 per cent. of the total boric acid. This shows the necessity of avoiding the boiling of an ammoniacal boric acid solution.

The digestion with ammonium chloride, using a reflux condenser to prevent the loss of boric acid, was tried, but it was impossible to get rid of the silica, alumina, and ammonium salt in this manner. Evaporation to dryness and ignition seemed to be the only way to make the silica and alumina insoluble and destroy the ammonium salt.

### THE USE OF LIME TO PREVENT THE VOLATILIZATION OF BORIC ACID DURING EVAPORATION.

It occurred to me that the loss of boric acid during the evaporation to dryness and subsequent ignition, might be avoided by the addition of lime. Therefore, after digesting the extract of the fusion with ammonium chloride in a flask connected with a reflux condenser, and removing the precipitate, I added lime obtained by the ignition of precipitated calcium carbonate, evaporated the whole to dryness in a platinum dish and ignited strongly. Soda in excess of the amount required by the lime, and twenty-five cc. of water were added and the whole digested for half an hour. When cool, the precipitate was removed and well washed with cold water. After concentrating the filtrate and allowing it to cool, sulphuric acid was carefully added to almost the neutral point; the precipitate that formed was filtered out, the solution made just acid and the boric acid then titrated.

The following table shows the results obtained from the brown tourmaline (No. 4), which according to the previous method (page 876) contained 9.97 per cent. of boric acid:

| | Weight of mineral (No. 4). | $\frac{N}{2}$NaOH. | $B_2O_3$. | |
|---|---|---|---|---|
| No. | Gram. | cc. | Gram. | Per cent. |
| 1 | 0.5000 | 2.9 | 0.05075 | 10.15 |
| 2 | 0.5000 | 3.0 | 0.0525 | 10.50 |
| 3 | 0.3000 | 1.6 | 0.0280 | 9.33 |
| 4 | 0.3000 | 1.75 | 0.03062 | 10.21 |

In these determinations the insoluble oxides were re-fused and the extract of the fusion added to that of the first.

To ascertain whether the $CaO.B_2O_3$, formed upon the addition of lime to the ammoniacal boric acid solution, was completely decomposed by the boiling with sodium carbonate, a weighed amount of borax was subjected to the same treatment as the extract of the fusion. That the $CaO.B_2O_3$ was entirely decomposed by the boiling with soda, is proved by this table.

| | Taken. | | Found. | | |
|---|---|---|---|---|---|
| | Volume of solution. | Weight of borax. | | $\frac{N}{2}$NaOH. | |
| No. | cc. | Gram. | $B_2O_3$. Gram. | cc. | $B_2O_3$. Gram. |
| 1 | 10 | 0.01 | 0.006924 | 0.4 | 0.007 |
| 2 | 10 | 0.01 | 0.006924 | 0.4 | 0.007 |
| 3 | 20 | 0.02 | 0.013848 | 0.8 | 0.014 |

A black tourmaline, in which, as previously shown, the boric acid amounted to 10.15 per cent., yielded 9.92 per cent. when subjected to the above treatment.

Datolite gave the following:

| No. | Weight of mineral. Gram. | $\frac{N}{2}$NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|---|
| 1 | 0.5000 | 5.4 | 0.0945 | 18.90 |
| 2 | 0.3000 | 3.3 | 0.05775 | 19.25 |

This same datolite, according to the method on page 876, contained 19.25 per cent. of boric acid.

By using barium hydroxide in place of the lime and sodium sulphate instead of the carbonate, the following results were obtained from the brown tourmaline (No. 4):

| No. | Weight of mineral. Gram. | $\frac{N}{2}$NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|---|
| 1 | 0.3000 | 1.3 | 0.02275 | 7.58 |
| 2 | 0.3000 | 1.8 | 0.0315 | 10.50 |
| 3 | 0.3000 | 1.6 | 0.0280 | 9.33 |
| 4 | 0.2770 | 1.5 | 0.02625 | 9.49 |
| 5 | 0.5000 | 2.6 | 0.0455 | 9.10 |
| 6 | 0.5000 | 2.4 | 0.0420 | 8.40 |

In this series, the insoluble oxides were not re-fused, but were dissolved in sulphuric acid and subjected to distillation with methyl alcohol, etc., whereupon the following percentages were obtained:

| No. | $\frac{N}{2}$NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|
| 1 | 0.2 | 0.0035 | 1.16 |
| 2 | 0.1 | 0.00175 | 0.58 |
| 3 | 0.1 | 0.00175 | 0.58 |
| 4 | 0.05 | 0.000875 | 0.29 |
| 5 | 0.1 | 0.00175 | 0.58 |

Upon igniting the distillate of No. 6, the characteristic green flame of boron was obtained. If these percentages are added to those previously obtained, it will be noticed that it makes the boric acid found in Nos. 3, 4, and 5 respectively 9.92 per cent., 9.80 per cent., and 9.45 per cent. These numbers agree fairly closely with those obtained from the same tourmaline by the method described on page 876. From the foregoing, the necessity of re-fusing the insoluble oxides in order to entirely remove the boric acid is apparent.

This method, while not giving results as reliable as that in which the boric acid is volatilized as the methyl ester, yet answers fairly well and avoids the use of complicated apparatus: the time is lessened very little if at all. If the digestion with ammonium chloride could be avoided, that is if the alumina could be separated from the boric acid by some other means, the evaporation to dryness and ignition might be unnecessary and thus the time shortened. In looking for a means of accomplishing this object, I happened upon the reaction $2AlO.ONa + CO_2 + 3H_2O = Al_2(OH)_6 + Na_2CO_3$, which is made use of in the manufacture of soda from cryolite. Hoping by this means to separate the alumina from the boric acid, I conducted carbon dioxide into the boiling solution of the sodium carbonate fusion free from the insoluble oxides. The separation, however, was not complete, as the following show:

| No. | Weight of mineral. Gram. | $\frac{N}{2}$NaOH. cc. | $B_2O_3$. Gram. | Per cent. |
|---|---|---|---|---|
| 1 | 0.5000 | 12.0 | 0.2100 | 42.00 |
| 2 | 0.3000 | 10.0 | 0.1750 | 58.33 |

The solutions, after titration, were found to contain large amounts of alumina.

By passing carbon dioxide through a cold solution of sodium aluminate, Day[1] completely separated all the alumina from the

[1] *Am. Chem. J.*, 19, 718.

soda. I then passed carbon dioxide through the cold fusion extract, as shown in this table:

| Time of conducting $CO_2$ through the solution. Hours. | Volume of solution. cc. | | | |
|---|---|---|---|---|
| 2.5 | 200 | a precipitate formed. | | |
| 2.0 | 300 | " | " | " |
| 1.0 | 350 | " | " | " |
| 2.0 | 500 | no | " | " |
| 7.5 total time. | | Temperature of solution 1° C. | | |

The solution was then evaporated to a small volume, and after the expulsion of all the carbon dioxide, titrated for boric acid.

| | Weight of mineral (No. 4). | $\frac{N}{2}$NaOH. | $B_2O_3$. | |
|---|---|---|---|---|
| No. | Gram. | cc. | Gram. | Per cent. |
| 1 | 0.3000 | 1.95 | 0.03413 | 11.34 |

After titration, upon boiling with hydrochloric acid and adding ammonia, a precipitate of alumina was obtained which weighed 0.0039 gram, equivalent to 1.3 per cent. of the mineral.

This procedure was then repeated with the following results:

| Time of conducting $CO_2$ through the solution. Hours. | Volume of solution. cc. | | | |
|---|---|---|---|---|
| 2.0 | 300 | a precipitate formed. | | |
| 4.6 | 400 | " | " | " |
| 1.0 | 500 | no | " | " |
| 7.0 total time. | | Temperature of solution, 1° C. | | |

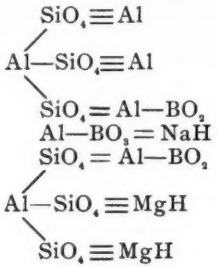
The treatment was as in the former case and 12.77 per cent. of boric acid was found. Upon testing the titrated solution for alumina, 0.0075 gram, equivalent to 1.5 per cent. of the mineral, was obtained.

In all attempts to determine the boric acid in tourmalines containing much alumina great difficulty has been experienced in separating the alumina from the boric acid and alkali carbonate. In following out Marignac's method, alumina is always found with the magnesium borate, magnesium chloride, and silica. The tenacity with which boron oxide and alumina hold to one another in other than acid solutions, is extremely great, as has already been demonstrated and is further shown by the following experiment:

0.1733 gram of aluminum, corresponding to 0.32565 gram of aluminum trioxide, was dissolved in hydrochloric acid and the

excess of acid expelled; 2.019 grams of fused borax and 1.0 gram of sodium carbonate dissolved in water, were added to the aluminum chloride and the whole boiled one hour. These proportions were taken from the equation $3H_2O + 3Na_2B_4O_7 + Al_2Cl_6 = Al_2(OH)_6 + 6NaCl + 2B_2O_3$. The precipitated alumina was well washed, dissolved in hydrochloric acid, reprecipitated by ammonia, ignited, and weighed. It equaled 0.2906 gram, or 89.23 per cent. of all the alumina present in the solution. The washings, after boiling to expel the ammonia, were added to the filtrate. The volume of the solution then equaled 400 cc., and when cooled to 1° C. carbon dioxide was conducted through it for fifteen hours. The precipitate was removed and treated as the first; it amounted to 0.0332 gram, or 11 plus per cent. of all the alumina. This with the former percentage equals 100.23 per cent. Carbon dioxide, passed through two hours longer, caused no further precipitation, yet upon acidifying, then adding ammonia, a precipitate was obtained which amounted to 0.0051 gram of aluminum trioxide, or 1.56 per cent. The total amount of aluminum trioxide was 0.32565 gram, while that estimated equaled 0.3289 gram. This excess is due beyond a doubt to the contamination of the precipitates with boric acid, although in all except this last instance the precipitates were dissolved in hydrochloric acid and reprecipitated by ammonia.

The obstinacy with which aluminum trioxide and boron trioxide cling together, it seems to me, would indicate the existence of a salt of aluminum and boron in this alkaline solution. This would also favor the view held by Clarke (Bulletin 125, United States Geological Survey), which he expresses in his structural formula for tourmaline.



The alumina, as is seen, links the boric acid to the silica. This view, I think, is further strengthened by the fact that calcium or barium carbonate, fused with borax, then boiled with sodium carbonate or sulphate, gave up all the boron trioxide to the alkali, while tourmaline, heated with calcium or barium carbonate, then boiled with carbonate or sulphate of soda, yielded to the alkali but a portion of the boric acid; the alumina most likely held the remainder.

## SUMMARY.

In order to avoid the introduction of alkalies, which, as it has been shown, are objectionable, new methods for the decomposition of the mineral were attempted. The first of these was the heating of the mineral with metallic magnesium and subsequently volatilizing the boron by heating in a stream of chlorine. From all appearances, the decomposition of the mineral was complete, but in the treatment with chlorine, either the boron was partially retained by the other chlorides formed at the same time, or if it was entirely volatilized as the chloride, it was not decomposed when it came in contact with the water saturated with chlorine. By using a large volume of water this difficulty might be avoided, but if the chlorine is removed by drawing air through the solution, some boric acid would be carried out with it. Again, if alkali is added, hypochlorite of the alkali would be formed, and this, when neutralized, would free chlorine, which again would likely carry with it boric acid, or the hypochlorous acid formed would cause trouble in the titration.

By fusing the mineral with calcium carbonate, also with barium carbonate, a complete decomposition was obtained, but the separation of the boric acid was incomplete. Some of the boric acid was held by the alumina, which was re-fused to yield it to the alkali with which the fusion was digested. This must be the case, since calcium or barium carbonate fused with borax, then boiled with sodium carbonate or sulphate, gave up all the boron trioxide. This strengthens the idea that the boron, which is so constant a quantity in tourmalines, is linked through the aluminum to the silica, probably as an aluminum metaborate, as Clarke suggests.

The mineral was then fused with alkali carbonates, and by volatilizing the boron from an acid solution as the methyl ester, the boron was successfully isolated and its estimation made by the volumetric method of Thompson. The use of a current of air with the apparatus described, shortens the time required for the volatilization of the ester, very materially. As has been shown, impure methyl alcohol prevents the complete volatilization of the boric acid. The results obtained by this method are reliable, and the method is capable of very wide application. The great affinity that alumina has for boric acid, has been pretty thoroughly demonstrated in the foregoing work, and the most successful means of overcoming this affinity and completely separating these two, is by volatilizing the boric acid from an acid solution. If an acid or ammoniacal borax solution is boiled, there is the likelihood of a very appreciable loss of boric acid; by this method there is no boiling of acid or ammoniacal solutions. These facts, and the brief time required for its performance, recommend this method for the estimation of boric acid in all silicates.

Could boric acid be separated from manganese, without volatilization, its estimation in silicates could be accomplished through the salt $MnO.2B_2O_3$. As has already been proved, the method is successful when applied to borax. If the attempt is made to remove the manganese with alkali, the precipitation is incomplete; if ammonium sulphide is used, the difficulties encountered are well known, and if the manganese is precipitated from an acid solution, boric acid is volatilized.

As has been shown, the volatility of boric acid in ammonia is very appreciable, hence any method in which an ammoniacal boric acid solution is boiled in the open, is unreliable, unless some substance is introduced to bind the acid. I have used lime for this purpose, and found it to fulfil its end.

By re-fusing the insoluble oxides with alkali carbonate, it is possible to separate the boric acid. However, I do not believe the separation is complete even then, but that the amount of boric acid left after the first fusion is so diluted by the second, that what remains with the insoluble oxides may be neglected. By twice fusing and digesting the extract with ammonium chloride with a reflux condenser, then evaporating the solution

to dryness with lime in a platinum dish and igniting the residue, the silica and alumina are made insoluble; then digestion with sodium carbonate gives borax in which the boric acid is readily titrated by the method of Thompson. This method works very well with alumina containing silicates; with datolite, better results were obtained. It avoids the use of complicated apparatus and requires for its execution about four hours. With silicates decomposable by digestion with acids[1] it seems to me, this would be the method.

The obstinacy that is encountered in separating alumina from boron trioxide in an alkaline solution, calls to my mind a point which I think is worthy of some attention. In the complete analysis of minerals, such as tourmaline, it is customary to evaporate the hydrochloric acid solution of the fusion to dryness, remove the silica and precipitate the iron and alumina from the filtrate as hydroxide by ammonia. Although these hydroxides have been dissolved in hydrochloric acid and reprecipitated, yet considerable difficulty is experienced in obtaining two determinations from the same sample that agree. This trouble I believe to be due to boric acid, which does not go off in the evaporation to dryness with hydrochloric acid. If this be true, this difficulty might be eliminated by the addition of methyl alcohol during the evaporation with hydrochloric acid.

The facts to which I have called attention in the latter part of this paper, argue strongly for the formula proposed by Clarke to represent the structure of tourmaline. But, as I have said, we know nothing of the magnitude of the molecule, hence such representations are surmises only. Until some means of ascertaining the size of the mineral molecule has been devised, such formulas will have to be looked upon with doubt.

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# AN ELECTROLYTIC STUDY OF BENZOIN AND BENZIL.[1]

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## INTRODUCTION.

AS is well known, there is a wide difference in the action of various oxidizing as well as reducing agents on organic compounds. Probably no better illustration could be given of this than the following, on the oxidation of aniline, from Lassar-Cohn's "Manual of Organic Chemistry:" "With manganese dioxide and sulphuric acid, aniline gives ammonia and very little quinone. Chromic acid mixture gives a quantitative yield of the latter. Potassium permanganate in alkaline solution gives azobenzene, ammonia, and oxalic acid. In acid solution it gives aniline black, which with more energetic oxidation, is converted into quinone. In neutral solution, nitrobenzene and azobenzene are the chief products. Boiling bleaching-powder solution likewise gives nitrobenzene. Hydrogen peroxide in presence of weak acids gives ammonia and dianilidobenzoquinone anilide. In presence of strong acids it seems to give an inuline derivative."

In like manner, there is a marked difference in effect between electrolytic oxygen and hydrogen and other oxidizing and reducing agents. And again, different degrees of oxidation or reduction by the current can be effected by variations in current density, concentration, temperature, etc.

To study the oxidizing and reducing action of the electric current on benzoin and benzil as compared with other agents, and to determine the result of working in different solutions as well as with variations in current density, concentration, and temperature, is the object of this investigation.

The apparatus with which the experiments were performed consisted of a beaker-glass, a porous cup, which separated the anode and cathode liquids, and platinum electrodes, each of 100 sq. cm. surface. When hydrochloric acid solutions were used the platinum anode was replaced by one of carbon.

When heat was applied in sufficient amount to evaporate the

[1] From author's thesis for the degree of Ph.D.

solvent, the top of the porous cup was closed by a rubber stopper, carrying, besides a heavy platinum wire to which was attached the electrode, a tube which led the vapor to a return condenser.

In some of the experiments with alkaline solutions the porous cup was replaced by a bag made of two thicknesses of heavy unbleached muslin, which had been previously soaked in concentrated caustic soda for twenty-four hours.

The outer liquid, whether an oxidation or reduction was being made, consisted of a solution of from ten per cent. to twenty per cent. of the same acid or alkali used in the inner cup.

The solvent generally used throughout this set of experiments was ninety-three per cent. ethyl alcohol. The concentration of the solutions was nearly always kept close to the point of saturation.

The current used for most of the work was that of the ordinary 110 volt incandescent light circuit; this was regulated by means of lamps and wire resistance, so that any current from one-tenth to ten amperes could be used. In a few instances the current from storage cells was used.

The melting-points given in the following work were taken with an ordinary thermometer and are not corrected.

## EXPERIMENTS ON THE ELECTROLYTIC OXIDATION OF TOLUENE.

Before taking up the work on the oxidation and reduction of benzoin, attempts were made to oxidize the methyl group in toluene by the action of electrolytic oxygen. These experiments were unsuccessful, but it is hoped that they may not be without some interest.

The toluene used was from Kahlbaum, and distilled constantly at 110°.

*Experiment I.*—

| | |
|---|---|
| 15 grams toluene. | $N.D._{100} = 0.05$ ampere. |
| 210 cc. alcohol. | Voltage = 60–70. |
| 15 grams sodium hydroxide. | Temperature, 20°. |
| 30 cc. water. | Time, 1 hour. |

On acidifying the cup contents with hydrochloric acid and filtering off the sodium chloride, the remaining liquid, on distillation, yielded nothing but alcohol, water, and toluene, together with a small amount of brown resin.

*Experiment II.*—

| | |
|---|---|
| 33 grams toluene. | $N.D._{100} = 0.05$ ampere. |
| 460 cc. alcohol. | Voltage $= 2\frac{1}{3}$. |
| 65 cc. water. | Temperature, 25°. |
| 30 grams sodium hydroxide. | Time, 1 hour. |

The alcohol was distilled from the anode liquid and hydrochloric acid added to acidulation. This acid liquid, on shaking with ether, gave nothing but toluene and a small amount of resinous material.

*Experiment III.*—

| | |
|---|---|
| 15.4 grams toluene. | $N.D._{100} = 0.25$ ampere. |
| 210 cc. alcohol. | Voltage = 40–50. |
| 15 grams sodium hydroxide. | Temperature, 20.5°. |
| 30 cc. water. | Time, 10 hours. |

There was no heat applied and the current produced no rise in temperature. The cup contents were acidified with hydrochloric acid and the sodium chloride which separated filtered off; subsequent distillation yielded only water, alcohol, and toluene, besides a small amount of brown resinous substance.

*Experiment IV.*—

| | |
|---|---|
| 63.7 grams toluene. | $N.D._{100}$ = varying. |
| 30 cc. acetone. | Voltage = varying. |
| Sodium hydrodixe to saturation. | Temperature, varying. |
| | Time, 2 hours. |

On connecting the poles in circuit it was found that this solution would not conduct the current, so one cc. of a saturated solution of sodium hydroxide was added. The current was started at a normal density of 4.25 amperes and voltage of 13; after fifteen minutes the heat developed by the current was sufficient to make the acetone boil violently. The current was lowered to two and five-tenths amperes, the acetone still continuing to boil. In one hour and twenty minutes the temperature in the outer cup was 68°, and twenty minutes later one cc. of a saturated solution of sodium hydroxide was added. At the end of two hours the amperage had fallen to one and the voltage stood at seventy.

The anode liquid, on distilling off the acetone, yielded nothing but a small amount of tarry substance. This experiment showed that acetone would not serve as a solvent.

*Experiment V.*—

| | |
|---|---|
| 42.5 grams toluene. | $N.D._{100} = 0.5$ ampere. |
| 20 grams sodium sulphate. | Voltage = 12–20. |
| 100 cc. alcohol. | Temperature, 25°. |
| | Time, 9½ hours. |

The alcohol and part of the toluene were removed by distillation and the anode liquid was then neutralized with barium carbonate. The neutral solution was shaken out with ether and this extract yielded, on fractionation, besides toluene, less than one cc. of a liquid of ester-like odor, which boiled between 39° and 44° under a pressure of twenty mm. The barium carbonate residue contained no organic products.

*Experiment VI.*—

| | |
|---|---|
| 42.5 grams toluene. | $N.D._{100} = 0.5$ ampere. |
| 50 cc. alcohol. | Voltage = 80. |
| 4 grams sodium sulphate. | Temperature, 75°. |
| | Time, 12 hours. |

The current heat held the temperature at 75°. After twelve hours a strong-smelling layer of brown oily liquid separated on the top of the solution in the porous cup. This, on being neutralized with sodium carbonate and shaken out with ether, gave on fractionation a small amount of a liquid similar in odor to that obtained in the previous experiment, and which distilled under twenty mm. pressure almost constantly at 35°. Too small an amount of this was obtained to determine its composition. The residual liquid gave no organic products on being reacidified.

*Experiment VII.*—

| | |
|---|---|
| 42.5 grams toluene. | $N.D._{100} = 1$ ampere. |
| 100 cc. alcohol. | Voltage = 40–50. |
| 10 grams ammonium sulphate. | Temperature, 75°–80°. |
| | Time, 9½ hours. |

During the electrolysis a very strong odor like that of impure acetamide was observed. After nine and one-half hours the current was interrupted and the upper oily layer which had separated, neutralized and dried over calcium chloride. On subjecting this liquid to fractionation, besides toluene and tarry matter, a very small amount of a sharp smelling substance was obtained, which distilled under seventy mm. pressure at 39°–42°.

It was then determined to increase the amperage, to see if a definite product could be obtained in some quantity.

*Experiment VIII.*—

| | |
|---|---|
| 42.5 grams toluene. | $N.D._{100} = 1.5$ amperes. |
| 100 cc. alcohol. | Voltage = 11–14. |
| 10 grams ammonium sulphate. | Temperature, 60°–65°. |
| | Time, $9\frac{1}{2}$ hours. |

As in the previous experiment, a strong odor like that of impure acetamide was observed. The anode liquid was neutralized by standing twelve hours over barium carbonate. On shaking out with ether and fractionating nothing but tarry products could be obtained. The residual liquid gave no organic products on being acidulated and shaken out with ether.

No further work was done in this direction, the oxidation of benzoin being taken up next.

Since a mixture of chromic and nitric acids readily oxidizes the methyl group in toluene to carboxyl, doubtless conditions can be found in which the same would be effected by electrolytic oxygen. The great obstacle in the above work was in obtaining a solvent that would give a solution of low resistance, and at the same time dissolve a sufficient amount of toluene. When such a solution is obtained the current density could certainly be found with which the desired oxidation would be accomplished.

## ELECTROLYTIC OXIDATION OF BENZOIN.

The benzoin for the following experiments was prepared by treating 230 grams of benzaldehyde with 460 grams alcohol, 46 grams potassium cyanide, and 115 grams water. This solution was boiled under a return condenser on the water-bath for one hour. The crystals which separated on cooling were washed with cold alcohol, treated with bone-black in boiling alcohol, and the solution filtered and recrystallized. The crystals thus prepared melted at 134°.

In the work with benzoin both the oxidizing and reducing effects of the current were studied.

*Oxidation of Benzoin in Alcoholic Sodium Hydroxide Solution.*—The first experiment was made with an alkaline alcoholic solution of benzoin, the conditions being taken at random.

*Experiment I.—*

| | |
|---|---|
| 5 grams benzoin. | $N.D_{100} = 0.75$ ampere. |
| 5 grams sodium hydroxide. | Voltage = 3.8 |
| 200 cc. alcohol. | Temperature, 60°. |
| | Time, 7 hours. |

It was found necessary with the above proportions to heat the alcohol to 60° in order to keep the benzoin in solution; this was done by placing the beaker containing the porous cup on a water-bath. At the end of seven hours the anode liquid had an acid-reaction. Hydrochloric acid was added to set free any organic acid that had been formed, and the liquid shaken out with ether. The ethereal extract, on evaporation, left a solid mass of an impure crystalline body. This was boiled up with barium carbonate and water, filtered, acidified, shaken out with ether, and the residue on sublimation gave crystals resembling benzoic acid, having a melting-point of 121.5°. An analysis of these crystals gave the following:

| Weight of substance in gram. | Weight of $CO_2$. | Per cent. C. | Per cent. C calculated for $C_6H_5COOH$. |
|---|---|---|---|
| 0.155 | 0.3875 | 68.11 | 68.85 |

| | Weight of $H_2O$. | Per cent. H. | Per cent. H calculated for $C_6H_5COOH$. |
|---|---|---|---|
| | 0.071 | 5.08 | 4.91 |

This identifies the body as benzoic acid, the oxidation proceeding according to the equation:

$$\begin{matrix} C_6H_5CO \\ | \\ C_6H_5CHOH \end{matrix} + O_2 = 2C_6H_5COOH.$$

Besides the benzoic acid there was a large quantity of tarry decomposition product formed in this as well as in the following experiments.

The benzoic acid obtained was not weighed and the following experiments, II to VII inclusive, were made to find the conditions giving the best yield of benzoic acid.

The quantity of sodium hydroxide was increased because, as was noted above, the cup contents had an acid-reaction at the close of Experiment I.

*Experiment II.—*

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 0.5$ ampere. |
| 10 grams sodium hydroxide. | Voltage = 4.5. |
| 200 cc. alcohol. | Temperature, 60°. |
| | Time, 7 hours. |

The anode liquid was still alkaline at the end of the time. The alcohol was evaporated, the residual liquid acidified with hydrochloric acid, shaken out with ether and the residue sublimed. A yield of sixteen per cent. of benzoic acid was obtained.

In the next experiment the amperage required by theory to convert all the benzoin to benzoic acid, was conducted through the solution.

*Experiment III.—*

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 0.5$ ampere. |
| 10 grams sodium hydroxide. | Voltage = 3.8. |
| 250 cc. alcohol. | Temperature, 60°. |
| | Time, 5 hours. |

The anode liquid subjected to the same treatment as before gave 9.6 per cent. of benzoic acid.

In the next experiment the time was shortened and a marked decrease in yield noted.

*Experiment IV.—*

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 0.5$ ampere. |
| 10 grams sodium hydroxide. | Voltage = 4.5. |
| 250 cc. alcohol. | Temperature, 60°. |
| | Time, 3 hours. |

The quantity of benzoic acid obtained was 8.2 per cent. In the next experiment the concentration was increased and the normal density lowered.

*Experiment V.—*

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 0.25$ ampere. |
| 10 grams sodium hydroxide. | Voltage = 2.8. |
| 150 cc. alcohol. | Temperature, 60°. |
| | Time, 7 hours. |

These conditions gave eighteen per cent. of benzoic acid, the largest yield obtained by oxidation in alkaline solution.

In the following experiment the concentration and normal density were made the same as above and the time shortened.

*Experiment VI.—*

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 0.25$ ampere. |
| 10 grams sodium hydroxide. | Voltage = 2.8 |
| 150 cc. alcohol. | Temperature, 60°. |
| | Time, 5 hours. |

The yield of benzoic acid in this case was 14.8 per cent.

To try the effect of higher amperage and longer time, both these factors were made twice as great as in Experiment V.

*Experiment VII.—*

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 0.5$ ampere. |
| 10 grams sodium hydroxide. | Voltage = 4–5. |
| 150 cc. alcohol. | Temperature, 60°. |
| | Time, 14 hours. |

The yield of benzoic acid obtained was 17.4 per cent. showing that no improvement was made by increasing time and normal density over that of Experiment V.

*Oxidation of Benzoin in Alcoholic Sulphuric Acid Solution.*

*Experiment I.—*

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 0.25$ ampere. |
| 5 grams sulphuric acid (conc.). | Voltage = 2.6. |
| 110 cc. alcohol. | Temperature, 60°. |
| | Time, 7 hours. |

On evaporating off about three-fourths of the alcohol from the anode liquid and cooling, crystallization set in. The crystalline mass was filtered off, washed with alcohol, redissolved in boiling alcohol and treated with bone-black; when cool, white crystals separated which gave a melting-point of 134°, proving the substance to be unchanged benzoin.

The concentration, time, and normal density were increased in the next experiment in order to effect the oxidation.

*Experiment II.—*

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 0.5$ ampere. |
| 5 grams sulphuric acid (conc.). | Voltage = 3.8. |
| 100 cc. alcohol. | Temperature, 60°. |
| | Time, 10 hours. |

The anode liquid was neutralized with sodium carbonate, after having the greater part of the alcohol removed by evaporation; a layer separated at this point having the odor of ethyl benzoate.

This ester layer was separated, and distilled between 200° and 215°; its saponification yielded benzoic acid. The lower layer after the removal of the ester was extracted with ether, the solvent evaporated, and the residue sublimed. This gave one and a half per cent. of benzoic acid, while the ester above held 15.8 per cent. in combination, making a total yield of 17.3 per cent.

The analysis of this acid gave the following:

| Weight of substance in gram. | Weight of $CO_2$. | Per cent. C. | Per cent. of C calculated for $C_6H_5COOH$. |
|---|---|---|---|
| 0.3960 | 0.9975 | 68.69 | 68.85 |
| | Weight of $H_2O$. | Per cent. of H. | Per cent. of H calculated for $C_6H_5COOH$. |
| | 0.181 | 5.07 | 4.91 |

The residue from the ether extract above was of a yellow color, which could be removed by chloroform, but on evaporation only a tarry mass was left.

The effect of an increase in normal density was tried in the next experiment, the other factors remaining the same.

*Experiment III.*—

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 1.5$ amperes. |
| 5 grams sulphuric acid (conc.). | Voltage = 9–10. |
| 100 cc. alcohol. | Temperature, 60°. |
| | Time, 10 hours. |

The anode liquid, worked up as before, gave for the total of free benzoic acid and that combined as ethyl benzoate only two and eight-tenths per cent. The quantity of tarry matter present was larger than in any previous experiment of this series.

*Oxidation of Benzoin in Alcoholic Hydrochloric Acid Solution.*—For the following experiments an anode of carbon was used together with a porous cup similar to that of the previous line of experiments. The outer liquid was a twenty per cent. hydrochloric acid solution. As benzoic acid resulted from the above oxidations, it was believed that it might be possible to prepare a chlorinated benzoic acid by working with a hydrochloric acid solution. The reaction, however, took a different course as the following experiments show:

*Experiment I.*—

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 1$ ampere. |
| 20 cc. hydrochloric acid (conc.). | Voltage = 2.3. |
| 100 cc. alcohol. | Temperature, 60°. |
| | Time, 9 hours. |

On account of the size of the carbon electrode the anode chamber was left open and the alcohol, that escaped by evaporation, replaced from time to time.

When the cup contents cooled, a mass of ill-defined crystals separated. The supernatant liquid was decanted, the mass washed with cold alcohol and dried. The substance was then sublimed, giving crystals resembling benzoic acid; these were subjected to two more sublimations, then dissolved in sodium carbonate, and reprecipitated; a final sublimation yielded crystals which melted at 121°. A yield of three and two-tenths per cent. of benzoic acid was obtained.

A small amount of a yellow solid separated from the supernatant liquid on the removal of the alcohol. This same yellow body separated from the benzoic acid at the point in its purification where it was treated with sodium carbonate solution. The two portions were combined, dissolved in alcohol, treated with bone-black, filtered, and recrystallized, giving a melting-point of 94°. Not enough of this body was obtained at this point for analysis, but as will be seen in the succeeding experiments, it proved to be benzil, and changes in the working conditions produced it with no accompanying yield of benzoic acid.

The analysis of the above acid gave the following:

| Weight of substance in gram. | Weight of $CO_2$. | Per cent. C. | Per cent. C calculated for $C_6H_5COOH$. |
|---|---|---|---|
| 0.165 | 0.420 | 69.83 | 68.85 |
| | Weight of $H_2O$. | Per cent. H. | Per cent. H calculated for $C_6H_5COOH$. |
| | 0.0825 | 5.58 | 4.91 |

*Experiment II.*—

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 2$ amperes. |
| 25 cc. hydrochloric acid (conc.). | Voltage = 3. |
| 150 cc. alcohol. | Temperature, 60°. |
| | Time, 12 hours. |

When the cup contents cooled some benzoin crystallized out. The liquid had a strong odor of ethyl acetate. On evaporating off the alcohol and ethyl acetate an oily substance separated, which solidified when the residual liquid cooled; this was removed, dissolved in alcohol, treated with bone-black, and allowed to crystallize; the body thus obtained gave a melting-point of 94°. The analysis of this body gave the following:

| Weight of substance in gram. | Weight of $CO_2$. | Per cent. of C. | Per cent. of C calculated for $C_{14}H_{10}O_2$. |
|---|---|---|---|
| 0.161 | 0.463 | 79.04 | 80.00 |

| | Weight of $H_2O$. | Per cent. of H. | Per cent. of H calculated for $C_{14}H_{10}O_2$. |
|---|---|---|---|
| | 0.0655 | 4.52 | 4.76 |

This analysis, together with the properties of the body, identify it as benzil, $C_{14}H_{10}O_2$. The oxidation in hydrochloric acid solution then proceeds according to the equation:

$$\begin{matrix} C_6H_5CO \\ | \\ C_6H_5CHOH \end{matrix} + O = \begin{matrix} C_6H_5CO \\ | \\ C_6H_5CO \end{matrix} + H_2O.$$

No benzoic acid could be found among the products of the oxidation.

*Experiment III.*—

5 grams benzoin.
60 cc. hydrochloric acid (conc.).
140 cc. alcohol.

$N.D._{100} = 3$ amperes.
Voltage = 2.7.
Temperature, 70°–75°.
Time, 10 hours.

The anode liquid worked up as in the preceding experiment gave seven and five-tenths per cent. of benzil, and a careful examination failed to show any benzoic acid.

In the next experiment the quantity of hydrochloric acid was decreased and the temperature raised to 75°–80°.

*Experiment IV.*—

5 grams benzoin.
25 cc. hydrochloric acid (conc.).
150 cc. alcohol

$N.D._{100} = 3$ amperes.
Voltage = 2.8–3.
Temperature, 75°–80°.
Time, 10 hours.

The porous cup was connected with an inverted condenser, yet at this temperature some of the alcohol escaped through the part of the cup above the line of the liquid, necessitating additions from time to time.

When the cup contents cooled, benzoin to the amount of thirty-one per cent. crystallized out. The yield of benzil in this experiment, based on the amount of benzoin decomposed, was 28.3 per cent.

The effect of increased normal density was tried in the following experiment:

*Experiment V.*—

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 6$ amperes. |
| 25 cc. hydrochloric acid (conc.). | Voltage = 4.3. |
| 150 cc. alcohol. | Temperature, 75°–80°. |
| | Time, 10 hours. |

As in Experiment IV considerable benzoin separated from the anode liquid on cooling. The yield of benzil here, based on the amount of benzoin decomposed, was sixty-two per cent.

The effect of a still greater normal density, together with an increase in the amount of hydrochloric acid, was tried in the next experiment.

*Experiment VI.*—

| | |
|---|---|
| 2.5 grams benzoin. | $N.D_{100} = 8$ amperes. |
| 50 cc. hydrochloric acid (conc.). | Voltage = 4.6. |
| 125 cc. alcohol. | Temperature, 68°. |
| | Time, 10 hours. |

No heat was applied to the solution, that developed by the current holding the temperature nearly constant at 68°. No benzoin remained over in this experiment and the yield of benzil was 75.4 per cent.

Since in none of the above experiments was there any chlorinated product, the following conditions were tried to prepare such a body:

*Experiment VII.*—

| | |
|---|---|
| 2.5 grams benzoin. | $N.D_{100} = 6$ amperes. |
| 100 cc. hydrochloric acid (conc.). | Voltage = 5–6. |
| 100 cc. alcohol. | Temperature, 65°–70°. |
| | Time, 19 hours. |

A dark brown pasty mass separated on cooling the anode liquid. The residual liquid after evaporation of the alcohol, deposited more of a similar material. Sublimation was tried with some of this tarry product, but no well-defined body could be obtained. Various attempts to isolate a definite product from this pasty mass resulted in failure.

## ELECTROLYTIC REDUCTION OF BENZOIN.

With the exception of a small quantity of a substance melting at 205°–206°, obtained both in hydrochloric and sulphuric acid solutions, the following experiments led to no definite results.

*Reduction of Benzoin in Alcoholic Sodium Hydroxide Solution.*

*Experiment I.*—

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 0.5$ ampere. |
| 5 grams sodium hydroxide. | Voltage = 3.6. |
| 150 cc. alcohol. | Temperature, 60°. |
| | Time, 10 hours. |

The cathode liquid was neutralized with hydrochloric acid, the alcohol removed by evaporation, some water added, and the whole shaken out with ether. The ethereal extract yielded a very small quantity of a white crystalline substance, which on purification melted with decomposition at 204°–210°.

*Experiment II.*—

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 4$ amperes. |
| 5 grams sodium hydroxide. | Voltage = 6–7. |
| 200 cc. alcohol. | Temperature, 70°–75°. |
| | Time, 15 hours. |

The above temperature was produced by the heating effect of the current alone. The cathode liquid was neutralized with hydrochloric acid, and the alcohol removed. From the residual liquid, on cooling, a yellow pasty substance separated together with a mass of white needle-like crystals resembling benzoic acid. The latter were separated, and purified by dissolving in sodium carbonate solution, reprecipitated by hydrochloric acid and sublimed; the product gave a melting-point of 121°, and agreed with benzoic acid in all its properties. The yield of benzoic acid was 4.9 per cent.

The yellow pasty substance resisted all attempts at crystallization, though all the solvents at hand were tried.

*Experiment III.*—

| | |
|---|---|
| 2.5 grams benzoin. | $N.D._{100} = 4$ amperes. |
| 5 grams sodium hydroxide. | Voltage = 7 |
| 100 cc. alcohol. | Temperature, 70°–78°. |
| 25 cc. water. | Time, 10 hours. |

The current heat in this experiment kept the temperature between 70° and 78°. A new porous cup was used and much trouble was caused by the accumulation of silicic acid between the anode and the cup. The current was stopped every two hours in order that this gelatinous mass might be removed.

The cathode liquid on standing over night separated into two layers; the whole was neutralized with hydrochloric acid and the alcohol evaporated. The residual liquid, on cooling, deposited a dark pasty mass, which on being removed dissolved in alcohol, imparting a purple color to the solution. It was found on evaporating this solution to crystallization, that a white flocculent mass separated, portions of which, exposed to the air, oxidized to a purple color like that of the alcoholic solution. Not enough of this material could be obtained in a pure state for analysis. The purple alcoholic liquid on complete evaporation left a blue mass which on sublimation gave benzoic acid.

*Experiment IV.*—

| | |
|---|---|
| 2.5 grams benzoin. | $N.D_{100} = 4$ amperes. |
| 5 grams sodium hydroxide. | Voltage = 4. |
| 100 cc. alcohol. | Temperature, 50°–55°. |
| | Time, 9 hours. |

The heat of the current kept the temperature between 50° and 55°.

Nothing separated from the cathode liquid on standing, but when neutralized with hydrochloric acid a flocculent precipitate separated; this was filtered off, washed with water to free it from sodium chloride, and dissolved in alcohol; several attempts were made to crystallize it, but this could not be effected. No well-defined body could be isolated from the filtrate above after the removal of the alcohol.

The formation of benzoic acid in Experiments II and III probably resulted from air oxidation of the unstable reduction products after their removal from the porous cup.

*Reduction of Benzoin in Alcoholic Sulphuric Acid Solution.*

*Experiment I.*—

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 1.5$ amperes. |
| 5 grams sulphuric acid (conc.). | Voltage = 3.6. |
| 100 cc. alcohol. | Temperature, 70°. |
| | Time, 10 hours. |

The cathode liquid was shaken out with ether, and this extract crystallized from alcohol after treatment with bone-black. After a second crystallization the body melted with decomposition at 235°. Not enough of this substance was obtained for analysis.

In the next experiment the temperature was increased.

*Experiment II.*—

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 1.5$ amperes. |
| 5 grams sulphuric acid (conc.). | Voltage = 4.6. |
| 100 cc. alcohol. | Temperature, 75°–78°. |
| | Time, 10 hours. |

A crystalline mass lined the sides of the vessel when the cathode liquid had cooled. A purification of this material yielded a very small amount of a white substance, consisting of minute crystals which melted between 205° and 206°. Such a small quantity of this body was obtained that the analytical results can have but little value. The figures obtained are as follows:

| Weight of substance in gram. | Weight of $CO_2$. | Per cent. C. | Weight of $H_2O$. | Per cent. H. |
|---|---|---|---|---|
| 0.0605 | 0.1945 | 87.66 | 0.0345 | 6.33 |

The simplest formula for this body would then be $C_{22}H_{19}O$.

In the third experiment of this series, the normal density was increased and also the quantity of sulphuric acid.

*Experiment III.*—

| | |
|---|---|
| 5 grams benzoin. | $N.D._{100} = 4.5$ amperes. |
| 20 grams sulphuric acid (conc.). | Voltage = 6.5. |
| 100 cc. alcohol. | Temperature, 75°. |
| | Time, 10 hours. |

The current heat was sufficient to keep up the temperature. At the end of the time, adhering to the cathode and cell wall, was a yellow pasty mass which was detached, and on purification gave crystals similar in appearance to those obtained in Experiment II, and having the same melting-point, 205°–206°. The alcoholic filtrate yielded a small additional amount of the same body. As before the quantity of pure substance obtained was too small for a reliable analysis. The combustion gave the following:

| Weight of substance in gram. | Weight of $CO_2$. | Per cent. C. | Weight of $H_2O$. | Per cent. H. |
|---|---|---|---|---|
| 0.034 | 0.161 | 88.63 | 0.014 | 4.57 |

These results approximate the formula $C_{22}H_{14}O$.

*Reduction of Benzoin in Alcoholic Hydrochloric Acid Solution.*

*Experiment I.—*

| | |
|---|---|
| 2.5 grams benzoin. | $N.D._{100} = 4.5$ amperes. |
| 25 cc. hydrochloric acid (conc.). | Voltage = 7. |
| 75 cc. alcohol. | Temperature, 75°. |
| | Time, 10 hours. |

An anode of carbon was used in this as in the other experiments of this series. The current heat was sufficient to keep up the temperature.

When the cathode liquid cooled, a small amount of a yellow material deposited, which on purification by bone-black and boiling alcohol gave a white crystalline body having a melting-point of 205°–206°. The mother-liquor from these crystals, and that decanted from the cup in the first place, when combined and concentrated, gave a yellow paste which could not be crystallized, though portions of it were tried with the various solvents.

The quantity of pure material above, which melted at 205°–206°, was too small to make a trustworthy analysis. The combustion gave the following:

| Weight of substance in gram. | Weight of $CO_2$. | Per cent. C. | Weight of $H_2O$. | Per cent. H. |
|---|---|---|---|---|
| 0.0458 | 0.1451 | 86.39 | 0.023 | 5.58 |

This analysis approximates the formula $C_{14}H_{11}O$.

ELECTROLYTIC OXIDATION OF BENZIL.

The benzil used in the following experiments was prepared according to the method given in Gattermann's "Practical Methods of Organic Chemistry." Crude benzoin was finely pulverized and heated in an open flask with frequent shaking, with twice its weight of pure concentrated nitric acid, for two hours on a rapidly boiling water-bath. When the oxidation was ended the reaction mixture was poured into cold water; after the mass solidified the nitric acid was poured off; it was then washed several times with cold water, pressed out on a porous plate and crystallized from alcohol. After filtering off the separated crystals, they were dried in the air on several layers of filter-paper. The crystals melted at 94°.

The experiments in this series were carried out in a manner nearly analogous to those with benzoin.

*Oxidation of Benzil in Alcoholic Sodium Hydroxide Solution.*

*Experiment I.—*

| | |
|---|---|
| 2.5 grams benzil. | $N.D._{100} = 0.5$ ampere. |
| 5 grams sodium hydroxide. | Voltage = 9. |
| 100 cc. alcohol. | Temperature, 40°–50°. |
| | Time, 10 hours. |

The heat developed by the current was sufficient to hold the temperature between the above limits.

After neutralization of the alkali, evaporation of the alcohol and extraction with ether, nothing but a tarry mass was obtained, from which nothing definite could be isolated.

*Experiment II.—*

| | |
|---|---|
| 2.5 grams benzil. | $N.D._{100} = 1$ ampere. |
| 5 grams sodium hydroxide. | Voltage = 9–45. |
| 100 cc. alcohol. | Temperature, 70°. |
| | Time, 6 hours. |

The current kept the solution heated to 70°. The resistance of the solution increased so that at the end of six hours the current was stopped, the voltage having risen to forty-five.

The solution, treated as in Experiment I, yielded nothing but tarry products.

*Experiment III.—*

| | |
|---|---|
| 2.5 grams benzil. | $N.D._{100} = 0.5$ ampere. |
| 5 grams sodium hydroxide. | Voltage = 2.2. |
| 75 cc. alcohol. | Temperature, 40°. |
| | Time, 6 hours. |

A muslin bag was used instead of the porous cup for this experiment and a marked lowering of the resistance effected. The current heat alone raised the temperature to 40°.

The anode liquid yielded nothing but undecomposed benzil and tarry decomposition products as before.

*Oxidation of Benzil in Alcoholic Sulphuric Acid Solution.*

*Experiment I.—*

| | |
|---|---|
| 2.5 grams benzil. | $N.D._{100} = 3$ amperes. |
| 20 grams sulphuric acid (conc.). | Voltage = 6.5°. |
| 100 cc. alcohol. | Temperature, 65°. |
| | Time, 10 hours. |

The above temperature was maintained by the current heat alone.

When the alcohol was evaporated from the dark-colored anode liquid the odor of ethyl benzoate was observed. The ester was not separated, but the whole was shaken out with benzene and ligroin, the solvent removed and the residual liquid treated with an excess of sodium hydroxide and subjected to the heat of the water-bath for several hours. After the saponification of the ester, the liquid was acidified, shaken out with a mixture of ether and benzene and the solvent evaporated; the sublimation of the residue yielded crystals resembling benzoic acid, having a melting-point of 121°. A yield of eight and seven-tenths per cent. was obtained and the analysis gave the following:

| Weight of substance in gram. | Weight of $CO_2$. | Per cent. C. | Per cent. C calculated for $C_6H_5COOH$. |
|---|---|---|---|
| 0.2442 | 0.6162 | 68.81 | 68.85 |
| | Weight of $H_2O$. | Per cent. H. | Per cent. H calculated for $C_6H_5COOH$. |
| | 0.1041 | 4.70 | 4.91 |

The reaction then proceeded according to the equation

$$\begin{matrix} C_6H_5CO \\ | \\ C_6H_5CO \end{matrix} + H_2O + O = 2C_6H_5COOH.$$

*Experiment II.*—

2.5 grams benzil
20 grams sulphuric acid (conc.).
100 cc. alcohol.

$N.D._{100} = 1$ ampere.
Voltage = 10.5.
Temperature, 65°.
Time, 10 hours.

No outside heat was applied, the current alone raising the temperature to 65° at the end of one and one-half hours.

On subjecting the anode liquid to the same treatment as in Experiment I, a yield of 14.5 per cent. benzoic acid was obtained.

*Oxidation of Benzil in Alcoholic Hydrochloric Acid Solution.*

*Experiment I.*—

5 grams benzil.
20 cc. hydrochloric acid (conc.).
75 cc. alcohol.

$N.D._{100} = 1$ ampere.
Voltage = 3.
Temperature, 60°.
Time, 10 hours.

Nothing but benzil separated when the cup contents cooled, and the alcoholic filtrate contained benzil and a small amount of tarry substance.

For the next experiment the normal density was increased to seven amperes.

*Experiment II.—*

| | |
|---|---|
| 5 grams benzil | $N.D._{100} = 7$ amperes. |
| 25 cc. hydrochloric acid (conc.). | Voltage = 6. |
| 100 cc. alcohol. | Temperature, 70°–75°. |
| | Time, 9 hours. |

Here again a crystalline mass of benzil separated when the anode liquid cooled. The alcoholic filtrate contained nothing but benzil and some tarry decomposition products.

## ELECTROLYTIC REDUCTION OF BENZIL.

### *Reduction in Alcoholic Sodium Hydroxide Solution.*

*Experiment I.—*

| | |
|---|---|
| 2.5 grams benzil. | $N.D._{100} = 0.5$ ampere. |
| 5 grams sodium hydroxide. | Voltage = 3.3. |
| 100 cc. alcohol. | Temperature, 30°. |
| | Time, 6 hours. |

A muslin bag was used for the porous septum in this experiment. The current kept the temperature at 30°.

The cathode liquor was neutralized with hydrochloric acid and the alcohol removed by evaporation. The residual liquid on cooling deposited a small amount of a white crystalline material, together with the unchanged benzil, which collected in a lump. The white crystals were readily soluble in cold alcohol and to a less degree in hot water. After a crystallization from hot water the crystals melted with some decomposition at 145°–146°. Not a sufficient quantity of this body was obtained for a combustion.

*Experiment II.—*

| | |
|---|---|
| 2.5 grams benzil. | $N.D._{100} = 3$ amperes. |
| 5 grams sodium hydroxide. | Voltage = 5. |
| 100 cc. alcohol. | Temperature, 50°. |
| | Time, 6½ hours. |

The current heat held the temperature at 50°. After neutralization with hydrochloric acid and removal of the alcohol, a small amount of white needle-like crystals separated, together with benzil and some tarry matter. The crystals were separated, dissolved in hot water, treated with bone-black, and recrystallized.

The body had no definite melting-point, beginning to fuse and decompose at 185°.

*Reduction of Benzil in Alcoholic Sulphuric Acid Solution.*

*Experiment I.*—

| | |
|---|---|
| 2.5 grams benzil. | $N.D._{100} = 4$ amperes. |
| 20 grams sulphuric acid (conc.). | Voltage = 9. |
| 100 cc. alcohol. | Temperature, 65°. |
| | Time, 15½ hours. |

No outside heat was applied, the current holding the temperature at 65°. On standing over night a small amount of a white crystalline substance separated, which was removed and purified, giving a melting-point of 205°–206°. The removal of the alcohol caused the deposition in small amount of a yellow, pasty mass, which oxidized very readily and could not be crystallized.

The white crystalline body above is probably the same as that obtained in several previous reductions. So little of these substances melting at 205°–206° was obtained in the various reductions that the analytical results have little value in establishing their identity, although the physical properties are the same. The white body obtained in this reduction analyzed as follows, approximating the formula $C_{28}H_{24}O$:

| Weight of substance in gram. | Weight $CO_2$. | Per cent. C. | Weight $H_2O$. | Per cent. H. |
|---|---|---|---|---|
| 0.048 | 0.161 | 91.46 | 0.0215 | 4.97 |

*Experiment II.*—

| | |
|---|---|
| 2.5 grams benzil. | $N.D._{100} = 1$ ampere. |
| 20 grams sulphuric acid (conc.). | Voltage = 4. |
| 100 cc. alcohol. | Temperature, 40°. |
| | Time, 10½ hours. |

The current heat alone kept up the temperature. When the current was interrupted it was found that a mass of white crystals lined the walls of the porous cup and adhered to the cathode. The crystals were washed with water, dissolved in alcohol, treated with bone-black and crystallized, melting sharply at 134°. When sublimed, these crystals suffered decomposition. In physical properties the body resembled benzoin and the analysis confirms this:

| Weight of substance in gram. | Weight of $CO_2$. | Per cent. C. | Per cent. C calculated for benzoin $C_{14}H_{12}O_2$. |
|---|---|---|---|
| 0.189 | 0.5495 | 79.28 | 79.24 |

| Weight of $H_2O$. | Per cent. H. | Per cent. H calculated for benzoin $C_{14}H_{12}O_2$. |
|---|---|---|
| 0.0985 | 5.78 | 5.66 |

The reaction then proceeds according to the equation:

$$\begin{matrix} C_6H_5CO \\ | \\ C_6H_5CO \end{matrix} + H = \begin{matrix} C_6H_5CO \\ | \\ C_6H_5CHOH \end{matrix}$$

The yield of benzoin obtained was 31 per cent.

*Reduction of Benzil in Alcoholic Hydrochloric Acid Solution.*

*Experiment I.*—

5 grams benzil.
20 cc. hydrochloric acid (conc.).
150 cc. alcohol.

$N.D._{100} = 1$ ampere.
Voltage = 2.2.
Temperature, 30°.
Time, 10 hours.

No external heat was applied. As with the sulphuric acid solution, there were white crystals hanging in masses to the cathode and the walls of the porous cup. These crystals were purified as in the above experiment and melted sharply at 134°. The alcoholic filtrate yielded more of the benzoin, making a total yield of 39 per cent. The analysis gave the following:

| Weight of substance in gram. | Weight of $CO_2$. | Per cent. C. | Per cent. C calculated for benzoin $C_{14}H_{12}O_2$. |
|---|---|---|---|
| 0.206 | 0.6075 | 80.42 | 79.24 |

| Weight of $H_2O$. | Per cent. H. | Per cent. H calculated for benzoin $C_{14}H_{12}O_2$. |
|---|---|---|
| 0.105 | 5.66 | 5.66 |

## SUMMARY.

*Comparison of the Above Results with those Obtained by the Usual Oxidizing and Reducing Agents.*

Benzoin, when treated with chromic acid, yields benzaldehyde and benzoic acid, while Fehling's solution, nitric acid, or chlorine oxidizes it to benzil.

The electrolytic oxidation in sodium hydroxide solution with normal density of 0.25 ampere gave the maximum yield of benzoic acid, while higher densities gave less acid and larger quantities of tarry decomposition products. With sulphuric acid solution the normal density had to be raised five-tenths ampere in order to effect oxidation, yet an increase in density here, as with the sodium hydroxide solution, gave more tarry matter and less benzoic acid.

In hydrochloric acid solution the experiment with normal density at one ampere gave as oxidation products both benzoic acid and benzil, while densities above this gave large yields of benzil alone, and an increase in both time and density factors gave only tarry decomposition products.

Sodium amalgam or benzoin yields hydrobenzoin together with a little isohydrobenzoin. Zinc and hydrochloric acid reduction of benzoin yields desoxybenzoin.

The experiments on the electrolytic reduction of benzoin gave as the only definite product the body melting at 205°–206°, which was obtained both in hydrochloric and sulphuric acid solutions.

The ordinary chromic acid oxidation of benzil yields benzoic acid.

With sodium hydroxide solution and densities of five-tenths and one ampere the electrolytic oxidation of benzil gave no definite products even when, as in one case, some benzil remained in the cup unchanged.

In sulphuric acid solution the electrolytic oxidation of benzil gave benzoic acid, 14.5 per cent. being the highest amount obtained.

With electrolytic oxygen in hydrochloric acid solution, benzil was unchanged when the normal density was equal to one ampere and an increase to seven amperes gave only a partial decomposition and indefinite tarry substances.

Benzil reduced by zinc and hydrochloric acid gives benzoin or desoxybenzoin according to the conditions.

The electrolytic reduction of benzil in sodium hydroxide solution gave nothing definite.

In sulphuric acid solution, benzil gave by the current reduction benzoin, the product crystallizing in an almost pure condition on the walls of the porous cup. An increase in the time factor gave besides decomposition products, a small amount of the body melting at 205°–206°, which is evidently the same as that obtained in the reduction of benzoin in both sulphuric and hydrochloric acid solutions.

By the current reduction in hydrochloric acid solution benzil gave benzoin in a crystalline form that was almost pure when taken from the cup.

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# ELECTROLYTIC DETERMINATIONS AND SEPARATIONS.

BY LILY G. KOLLOCK.[1]

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## INTRODUCTION.

THAT the electric current has greatly aided in the development of new and reliable methods for the determination and separation of metals is no longer questioned. That new material will continue to be added to what we now possess is also certain to occur. But in the old methods, worked out long before correct ideas prevailed as to current density, concentration of the solution and electrode surface, gaps exist, and uncertainty must necessarily prevail in the minds of those who seek to reproduce the proper working conditions of these earlier methods. That the latter are in every sense satisfactory in the hands of those persons who are thoroughly acquainted with them is also beyond question. To render them, however, universally acceptable, and to render their place in analytical chemistry by electrolysis permanent, the absolute conditions for successful work on the part of any investigator, must be definitely established. To this end a number of the earlier methods in which the double cyanides were used as electrolytes have been carefully reviewed in the following pages, and the conditions of current density, amperage, voltage, and other factors fully worked out. Thus edited, doubt can no longer be thrown upon the methods proposed, and they will continue to be in their developed condition the most reliable for the purposes for which they have been suggested. They now for accuracy, neatness, and rapidity of execution most certainly excel the ordinary gravimetric and volumetric methods applied to the same metals.

## CADMIUM.

In 1878 Smith showed that cadmium could be precipitated quantitatively from its alkaline double cyanide solution. In the following experiments cadmium sulphate containing 0.1659 gram cadmium in ten cc. was converted into the double cyanide, using

[1] From author's thesis for the degree of Ph.D.

one gram of potassium cyanide. The solution was electrolyzed with a current $N.D._{100} = 0.04\text{–}0.06$ A and $V = 2.9\text{–}3.2$. The solution was heated to 60° C. After the current had passed for six hours, the deposit was washed with hot water and alcohol, dried and then weighed. The solution poured out of the platinum dish, and examined qualitatively for cadmium, showed that all the cadmium had been deposited in this time. It was likewise entirely precipitated when the current was allowed to act on the solution through the night in the cold. The following results were obtained :

RESULTS.

| Cadmium. Gram. | Potassium cyanide. Gram. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. | Metal found. Gram. |
|---|---|---|---|---|---|---|---|
| 0.1659 | 1 | 125 | $N.D._{100}=0.06$ A. | 2.9 | 57° | 7 hours | 0.1657 |
| 0.1659 | 1 | 125 | $N.D._{100}=0.04$ A. | 2.9 | cold | during night | 0.1650 |
| 0.1659 | 1 | 125 | $N.D._{100}=0.06$ A. | 3.2 | 60° | 3 hours | 0.1655 |

## SILVER.

It is stated[1] that silver may be precipitated from a cyanide solution containing an excess of potassium cyanide. It may be deposited with a low current, and has the advantage of non-precipitation of silver peroxide at the anode.

Accordingly a silver nitrate solution containing 0.1270 gram of silver in 25 cc., after the addition of 0.5 gram of potassium cyanide, was diluted to 125 cc. This solution was electrolyzed with a current $N.D._{100} = 0.07$ A and $V = 3.2$. The temperature was 65° C. The deposition was complete in three hours. With a current of $N.D._{100} = 0.1$ A the silver was deposited completely in two hours. The relation between the current and the time factor may be seen in the following table :

RESULTS.

| Silver. present. Gram. | Potassium cyanide. Gram. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Found. Gram. |
|---|---|---|---|---|---|---|---|
| 0.1270 | 0.5 | 100 | $N.D._{100}=0.07$ A. | 3.2 | 65° | 3 | 0.1271 |
| 0.1270 | 0.5 | 100 | $N.D._{100}=0.07$ A. | 3.2 | 65° | 3 | 0.1270 |
| 0.1270 | 0.5 | 100 | $N.D._{100}=0.06$ A. | 3.2 | 65° | 3 | 0.1273 |
| 0.1270 | 1 | 100 | $N.D._{100}=0.01$ A. | 3 | 65° | 2 | 0.1268 |
| 0.1026 | 1 | 100 | $N.D._{100}=0.04$ A. | 2.5 | 65° | 5 | 0.1026 |
| 0.1026 | 1 | 100 | $N.D._{100}=0.04$ A. | 2.5 | 65° | 5 | 0.1024 |

[1] Smith's Electro-Chemical Analysis, p. 77.

## SEPARATIONS.

*Silver from Platinum.*—Smith[1] described this separation. A current of one cc. of oxy-hydrogen gas per minute acted upon a solution of the double cyanide produced by adding two and five-tenths grams of potassium cyanide. The silver was deposited free from any trace of platinum.

The separation, therefore, was taken up in order to get the exact working conditions. The salts of the metals used were silver nitrate containing 0.1026 gram of silver, and platinic chloride containing from 0.0879 gram to 0.1758 gram of platinum. To the combined solutions 1.25 grams of potassium cyanide were added and the whole diluted to 125 cc. The current used was $N.D._{100} = 0.04$ A and $V = 2.5$ The temperature was 70°. In from three to four hours the current was interrupted and the deposit washed with hot water and alcohol. It was found to be free from platinum. The filtrate gave no reaction for silver.

RESULTS.

| Silver. Gram. | Platinum. Gram. | Potassium cyanide. Gram. | Current. | Voltage. | Temperature. | Dilution. cc. | Time. Hours. | Found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1026 | 0.879 | 0.5 | $N.D._{100}$=0.05 A. | 2.5 | 78° | 125 | 5 | 0.1030 |
| 0.1026 | 0.1758 | 1.25 | $N.D._{100}$=0.05 A. | 2.5 | 75° | 125 | 3 | 0.1022 |
| 0.1026 | 0.1758 | 1.25 | $N.D._{100}$=0.45 A. | 2.4 | 75° | 125 | 3 | 0.1028 |
| 0.1026 | 0.1758 | 1.25 | $N.D._{100}$=0.04 A. | 2.5 | 75° | 125 | 3 | 0.1025 |
| 0.1026 | 0.1758 | 1.25 | $N.D._{100}$=0.04 A. | 2.5 | 75° | 125 | 3 | 0.1025 |

*Silver from Copper.*—In the *American Chemical Journal*,[2] there appears a series of forty experiments relating to the separation of these metals. Copper was found to have been precipitated with the silver when the deposition took place from a cyanide solution. It was then thought that copper could not be separated from silver by this method. In 1889 a set of new experiments was reported. By lowering the strength of the current the separation was made. The silver deposit contained no copper nor could silver be detected in the copper solution poured from the dish. In 1895 Smith and Wallace published a report of the separation made in that year.

I found that the following conditions gave accurate results. The solution of silver nitrate used contained 0.1024 gram of

[1] *Am. Chem. J.*, 13, 417.
[2] *Ibid.*, 11, 264.

metal and that of copper nitrate contained 0.0998 gram of copper. To the mixed solution two grams of potassium cyanide were added. The liquid containing an excess of potassium cyanide was diluted to 125 cc. This was subjected to a current of $N.D._{100} = 0.03–0.05$ A and $V = 1.1–1.66$. The current acted from three to seven hours. The deposit of silver was free from copper.

The results varied from the theoretical by 0.0002–0.0003 gram.

RESULTS.

| Silver. Gram. | Copper. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1024 | 0.0998 | 2 | 125 | $N.D._{100}=0.03$ A. | 1.16 | cold | 10 | 0.1027 |
| 0.1024 | 0.1 | 2 | 125 | $N.D._{100}=0.05$ A. | 1.1 | 65° | 7 | 0.1026 |
| 0.1024 | 0.1 | 1 | 125 | $N.D._{100}=0.058$ A. | 1.66 | 65° | 3 | 0.1026 |

*Silver from Cadmium.*—Smith and Spencer[1] found that the deposition of silver was accelerated by heating the solution during the electrolysis, and that while cadmium may be entirely precipitated in the cold by the current, yet with a low current and a temperature of 60° the cadmium is held in solution. A separation of silver and mercury may thus be effected in a cyanide solution. In the same journal, Smith and Frankel record the separation of mercury from cadmium, zinc, nickel, and cobalt. In 1895 Smith and Wallace published later results with the same method. Following the data thus obtained, a solution of silver nitrate containing 0.1024 gram of silver and cadmium sulphate solution equivalent to 0.168 gram of cadmium was used. The salts were transformed into their double cyanides by an excess of potassium cyanide. The silver was obtained free from cadmium in four hours. The current used was $N.D._{100} = 0.02$ A and $V = 2.15$. The temperature was 60° before the current was passed through the solution.

RESULTS.

| Silver. Gram. | Cadmium. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1024 | 0.168 | 2 | 125 | $N.D._{100}=0.02$ A. | 2.15 | 75° | 4 | 0.1025 |
| 0.1024 | 0.168 | 2 | 125 | $N.D._{100}=0.02$ A. | 2.1 | 60° | 4 | 0.1020 |
| 0.1024 | 0.168 | 2 | 125 | $N.D._{100}=0.025$ A. | 2.15 | 65° | 5 | 0.1027 |

The silver in all cases was found free from cadmium.

[1] This Journal, 16, 420.

*Silver from Zinc.*—These metals were separated according to the following conditions: Using zinc sulphate containing one-tenth gram of zinc and silver nitrate solution containing 0.1024 gram of silver. The potassium cyanide used amounted to one gram. The solution was 125 cc. in volume. It was electrolyzed at 70° by a current of $N.D._{100} = 0.032–0.038$ A and $V = 2.76$. In three hours the deposition of the silver was complete.

RESULTS.

| Silver. Gram. | Zinc. Gram. | Potassium cyanide. Gram. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1024 | 0.1 | 1 | 100 | $N.D._{100}=0.33$ A. | 2.76 | 60° | 3 | 0.1026 |
| 0.1024 | 0.1 | 1 | 100 | $N.D._{100}=0.38$ A. | 2.73 | 70° | 3 | 0.1028 |
| 0.1024 | 0.1 | 1 | 100 | $N.D._{100}=0.38$ A. | 2.70 | 65° | 3 | 0.1027 |

Nickel and cobalt were separated from silver in a similar way.

*Silver from Nickel.*—A solution of nickel nitrate containing one-tenth gram of nickel was added to a silver nitrate solution and both converted into the double cyanides by one and five-tenths grams of potassium cyanide. The solution was electrolyzed with a current $N.D._{100} = 0.02–0.03$ A and $V = 1.7–2$ for three hours. The separation in this time was found to be complete. The results show a variation from the calculated amount of +0.0001 gram to —0.0002 gram. The solution of silver in nitric acid, wnen examined qualitatively, gave no evidence of the presence of nickel. The nickel solution, when examined, showed that the silver had been entirely precipitated.

RESULTS.

| Silver. Gram. | Nickel. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1024 | 0.1 | 1.5 | 125 | $N.D._{100}=0.02$ A. | 1.7 | 65° | 3 | 0.1026 |
| 0.1024 | 0.1 | 1.5 | 125 | $N.D._{100}=0.03$ A. | 2. | 65° | 5 | 0.1025 |
| 0.1024 | 0.1 | 1.5 | 125 | $N.D._{100}=0.03$ A. | 1.66 | 60° | 3 | 0.1025 |

*Silver from Cobalt.*—Cobalt nitrate was the salt used in this separation. To the solution of silver nitrate (0.1024 gram of silver) was added a solution of the cobalt salt containing 0.1 gram of cobalt and 2.75 grams of potassium cyanide. A current of $N.D._{100} = 0.02$ A and $V = 2.2–2.7$ at a temperature of 65° was passed through the solution for five hours. The silver in this time was entirely precipitated. No cobalt was found deposited with the silver.

RESULTS.

| Silver. Gram. | Cobalt. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1024 | 0.1 | 2.75 | 125 | $N.D._{100}$=0.038 A. | 2.2 | 65° | 5 | 0.1028 |
| 0.1024 | 0.1 | 3.5 | 125 | $N.D._{100}$=0.02 A. | 2.2 | 65° | $3\frac{1}{2}$ | 0.1027 |

*Silver from Iron.*—Heretofore these metals have not been separated electrolytically in cyanide solution. A solution of ferrous ammonium sulphate, equivalent to one-tenth gram of metallic iron, was treated with sulphurous acid in order to reduce any ferric iron which might exist. After the reduction was complete the excess of acid was nearly neutralized with potassium carbonate; to this two and five-tenths grams of potassium cyanide were added. The solution of the double cyanide, dark green in color, was added to a solution of silver which had been converted into the double cyanide by five-tenths gram of potassium cyanide. The entire solution was made up to 100 cc. It was heated to 65° and electrolyzed with a current of $N.D._{100}$ = 0.04 A and V = 2.7. At the expiration of three hours the silver was found to be entirely deposited. There was in some cases a separation of ferric oxide at the anode. The silver, after its solution in nitric acid, was tested for iron by ammonium thiocyanate. A faint pink color, due to a trace of iron in the acid used for the solution of the metal, was observed. The deposit, which was light gray in color, varied but slightly from the theoretical amount of the silver present in the solution.

RESULTS.

| Silver. Gram. | Iron. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1002 | 0.1 | 3 | 125 | $N.D._{100}$=0.025 A. | 1.8 | 65° | 4 | 0.1001 |
| 0.1002 | 0.1 | 2.5 | 125 | $N.D._{100}$=0.02 A. | 1.8 | 70° | 4 | 0.1005 |
| 0.1002 | 0.1 | 3.25 | 125 | $N.D._{100}$=0.038 A. | 2.2 | 65° | 3 | 0.1000 |
| 0.1174 | 0.1 | 3 | 125 | $N.D._{100}$=0.04 A. | 2.25 | 70° | 3 | 0.1176 |
| 0.1174 | 0.2 | 4 | 125 | $N.D._{100}$=0.04 A. | 2.2 | 70° | 3 | 0.1174 |
| 0.1174 | 0.1 | 3 | 125 | $N.D._{100}$=0.05 A. | 2.2 | 75° | 3 | 0.1175 |

## MERCURY.

It is recorded[1] that mercury may be separated without difficulty with a low current and a large excess of alkaline cyanide. The deposits are noted as "compact, rather gray in color, and

[1] *Am. Chem. J.*, 11, 264.

showed in a few cases a drop-like nature so characteristic of mercury." The time required for the deposition under the conditions given was twelve to fourteen hours. Smith and Wallace,[1] published a number of separations of mercury from other metals—zinc, cadmium, cobalt, and nickel. The time required for separation was reduced to three and three and one-half hours.

In the experiments made this year the following conditions gave good results and confirmed those previously made. A solution of mercuric chloride, containing 0.1439 gram of mercury in ten cc. and five-tenths gram of potassium cyanide, was diluted to 100 cc. It was electrolyzed with a current $N.D._{100} = 0.07$ A and $V = 3.2$. The temperature of the solution was 65° C. In three hours the metal was completely deposited. The deposit was washed with slightly warm water.

RESULTS.

| Mercury. Gram. | Potassium cyanide. Gram. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Mercury found. Gram. |
|---|---|---|---|---|---|---|---|
| 0.1439 | 0.5 | 100 | $N.D._{100}$=0.07 A. | 3.2 | 65° | 3½ | 0.1441 |
| 0.1439 | 0.5 | 100 | $N.D._{100}$=0.07 A. | 3.2 | 65° | 3½ | 0.1442 |
| 0.1439 | 0.5 | 100 | $N.D._{100}$=0.02 A. | 1.6 | 65° | 6 | 0.1440 |
| 0.1439 | 0.5 | 100 | $N.D._{100}$=0.07 A. | 3.1 | 65° | 3 | 0.1436 |

The deposits obtained were light gray in color and were easily washed. They were bright and metallic in appearance, with higher voltage.

SEPARATIONS.

*Mercury from Copper.*—Smith and Frankel[2] report the separation of mercury and copper in an alkaline cyanide solution. A current generating two cc. of oxyhydrogen gas per minute was used for this purpose. The solution used contained 0.1833 gram of mercury and 14–70 per cent. of copper were added. With a current generating three and two-tenths cc. of oxyhydrogen gas, mercury was completely deposited in sixteen hours. It is stated, however, that when the quantity of copper present exceeded twenty per cent. the results were unsatisfactory. Later Smith and McCauley took up the separation again and by careful regulation of the current, were enabled to effect it even when the metals were present in equal quantities.

[1] This Journal, 17, 612.
[2] *Am. Chem. J.*, 11, 264.

In repeating this work a solution of mercuric chloride equivalent to 0.1216 gram of mercury and a copper sulphate solution, equivalent to one-tenth gram of copper were used. An excess of potassium cyanide was added. The entire solution was diluted to 125 cc. The current acting upon the solution was $N.D._{100} = 0.04$ A and $V = 1.09$. The temperature was 65°. In from two to four hours the mercury was completely deposited. On testing the metal qualitatively, the deposit was found free from copper.

RESULTS.

| Mercury. Gram. | Copper. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Merc'y found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1216 | 0.1 | 2.0 | 125 | $N.D._{100}=0.02$ A. | 1.09 | cold | 16 | 0.1220 |
| 0.1216 | 0.1 | 2.5 | 125 | $N.D._{100}=0.03$ A. | 1.9 | 65° | 4 | 0.1216 |
| 0.1216 | 0.15 | 3.5 | 125 | $N.D._{100}=0.035$ A. | 1.8 | 65° | 2½ | 0.1213 |
| 0.1216 | 0.1 | 3.0 | 125 | $N.D._{100}=0.04$ A. | 1.9 | 65° | 3 | 0.1215 |

*Mercury from Nickel.*—These metals were separated in an analogous manner to that described under the separation of silver from nickel. To the solutions of mercuric chloride and nickel nitrate were added two grams of potassium cyanide. This was then diluted to 125 cc. A current of $N.D._{100} = 0.04$ A and $V = 2.2$ was allowed to act for three hours. The deposit was found to weigh 0.0003 gram less than the calculated amount of mercury present. The filtrate was found to contain no mercury. No nickel was deposited with the metal.

RESULTS.

| Mercury. Gram. | Nickel. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Merc'y found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1216 | 0.1 | 2 | 125 | $N.D._{100}=0.04$ A. | 1.7 | 65° | 4 | 0.1220 |
| 0.1216 | 0.1 | 2 | 125 | $N.D._{100}=0.04$ A. | 2.2 | 65° | 4 | 0.1220 |
| 0.1216 | 0.15 | 2.5 | 125 | $N.D._{100}=0.04$ A. | 2.2 | 65° | 4 | 0.1211 |
| 0.1216 | 1 | 2 | 125 | $N.D._{100}=0.04$ A. | 2.2 | 65° | 4 | 0.1213 |

*Mercury from Cobalt.*—The mercuric chloride used in this separation contained 0.1216 gram of mercury and the cobalt nitrate contained one-tenth gram of cobalt. Two grams of potassium cyanide were added to the mixed solutions which were diluted to 100 cc. The current acting was $N.D._{100} = 0.03$ A and $V = 2.9$. With a temperature of 60° the deposition of the mercury was complete in five hours. It was free from cobalt.

RESULTS.

| Mercury. Gram. | Cobalt. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Merc'y deposited. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1216 | 0.1 | 2 | 100 | $N.D._{100}=0.025$ A. | 2.45 | cold | 16 | 0.1217 |
| 0.1216 | 0.1 | 2 | 100 | $N.D._{100}=0.025$ A. | 2.06 | 65° | 5 | 0.1213 |
| 0.1158 | 0.1 | 2 | 100 | $N.D._{100}=0.03$ A. | 2.9 | 65° | 5 | 0.1152 |

*Mercury from Zinc.*—The results obtained in the separation of mercury from zinc were first reported by Smith and Frankel in 1889. The electrolysis took place at the ordinary temperature in sixteen hours, with a current generating three cc. of oxyhydrogen gas per minute.

In the experiments made this year the following conditions gave satisfactory results.

RESULTS.

| Mercury. Gram. | Zinc. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1158 | 0.1 | 2 | 125 | $N.D._{100}=0.05$ A. | 3 | 60° | 4 | 0.1152 |
| 0.1158 | 0.1 | 1.5 | 125 | $N.D._{100}=0.033$ A. | 2.5 | 50° | 4 | 0.1155 |
| 0.1158 | 0.2 | 2 | 125 | $N.D._{100}=0.025$ A. | 2.9 | 50° | 4 | 0.1155 |

In the third determination the current acted for three hours at 50°, and then all night in the cold. The deposit in all cases was gray and compact. The mercury on examination for zinc gave no reaction for that metal, while no mercury was found in the zinc solution.

*Mercury from Cadmium.*—As stated under the separation of silver from cadmium, Smith and Wallace[1] found that cadmium might be separated from both silver and mercury by keeping the temperature slightly elevated. Unless this precaution is taken cadmium is precipitated with both metals, even when a low current is used.

The following proved to be good working conditions: The mercuric chloride solution used contained 0.1182 gram of mercury, and the cadmium sulphate solution was equivalent to 0.2206 gram of cadmium. The double alkaline cyanides were produced by the addition of two and one-half grams of potassium cyanide. A current of $N.D._{100}=0.018$ A and $V=1.7$ was passed through the solution, previously heated to 65° for seven hours. The mercury deposit was free from cadmium and weighed 0.1181 gram, which was 0.0001 gram lighter than the

[1] This Journal, 17, 612.

theoretical amount of mercury. It was repeatedly found that when the current was greater than 0.02 A, cadmium was precipitated.

*Mercury from Platinum.*—This separation was first carried out and reported by Smith.[1] The deposit of mercury was effected by using a current generating two cc. of oxyhydrogen gas a minute. The alkaline cyanide used for 0.1902 gram of mercury was two and a half grams. According to these suggestions a separation of the two metals was made. The mercury in solution was 0.1373 gram, and the platinum in the platinic chloride contained from 0.025 gram to 0.1 gram. In four hours the separation was completed. The current was $N.D._{100} = 0.05$ A and V = 2.1–2.3. The results show an error of —0.0001 gram to + 0.0003 gram.

RESULTS.

| Mercury Gram. | Platinum. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Merc'y deposited. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1373 | 0.025 | 3 | 125 | $N.D._{100}$=0.05 A. | 2.12 | 65° | 4 | 0.1372 |
| 0.1373 | 0.01 | 3 | 125 | $N.D._{100}$=0.04 A. | 2.12 | 75° | 4 | 0.1376 |
| 0.1373 | 0.01 | 3 | 125 | $N.D._{100}$=0.045 A. | 2.12 | 70° | 4 | 0.1375 |

*Mercury from Iron.*—The separation of mercury from iron, like that of silver from iron, has not been previously attempted in alkaline cyanide solution. Accordingly the following method was developed and found to yield satisfactory results:

The solution of the cyanide of iron was prepared from ferrous ammonium sulphate in precisely the same way as that described in the separation of silver from iron. The mercuric chloride solution contained 0.1216 gram of mercury. The cyanide present was from one to three grams, and the current was $N.D._{100} = 0.05$ A and V = 2.5. The temperature during the electrolysis was maintained at 70° C. In three hours the mercury was completely deposited. It was free from iron. The mercury deposit was dissolved in concentrated nitric acid. After diluting, a few crystals of ammonium thiocyanate were added. A faint pink color was observed, which was found to be due to the small trace of iron in the nitric acid.

[1] *Am. Chem. J.*, 13, 417.

RESULTS.

| Mercury. Gram. | Iron. Grams. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Merc'y deposited. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1216 | 0.1 | 1 | 100 | $N.D._{100}$=0.05 A. | 2. | 70° | 3 | 0.1215 |
| 0.1216 | 0.3 | 3 | 100 | $N.D._{100}$=0.04 A. | 2. | 70° | 4 | 0.1217 |
| 0.1216 | 2.5 | 2.5 | 100 | $N.D._{100}$=0.02 A. | 2.7 | 65° | 4 | 0.1217 |

## GOLD SEPARATIONS.

Smith and Muhr[1] report the separation of gold from palladium, platinum, zinc, cobalt, nickel, and copper.

*Gold from Palladium.*—It has been previously shown that palladium is not deposited with a current of 0.01 A in the presence of an excess of potassium cyanide. With a current liberating eight-tenths cc. of oxyhydrogen gas a minute, and the solution containing one and five-tenths grams of potassium cyanide, 0.1162 gram of gold was deposited in from twelve to fourteen hours.

In accordance with this suggestion, the following conditions were obtained: Two grams of potassium cyanide were added to a solution of gold chloride containing 0.1256 gram of metal and palladium chloride equivalent to one-tenth gram of metallic palladium. This was diluted to 250 cc. The current used was $N.D._{175}$ = 0.06–0.09 A and V = 1.5. The temperature during the decomposition was 65°. In five hours the current was raised to 0.09 A. The gold was found to be completely deposited and free from palladium.

RESULTS.

| Gold. Gram. | Palladium. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Gold found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1256 | 0.1 | 2 | 125 | $N.D._{100}$=0.06–0.03 A. | 2.5 | 65° | 6 | 0.1250 |
| 0.1256 | 0.1 | 2 | 250 | $N.D._{175}$=0.06–0.09 A. | 2.5 | 65° | 6 | 0.1257 |

*Gold from Copper.*—In the report referred to, the separation of gold from copper in cyanide solution took place with a current liberating eight-tenths cc. of oxyhydrogen gas at the ordinary temperature in about twelve hours.

It was found that by heating the solution to 65° the precipitation was more rapid, but required more cyanide in order to keep the copper from being deposited with the gold. To a solution of gold chloride containing 0.1665 gram of metallic gold and cop-

[1] *Am. Chem. J.*, 13, 417.

per sulphate containing one-tenth gram of copper, were added four grams of potassium cyanide. The solution (250 cc.), warmed to 65°, was electrolyzed with a current of $N.D._{.175} = 0.05$–0.07 A and $V = 1.7$ for two and one-half hours. In this time 0.1667 gram of gold was obtained. There was no reaction for copper when the deposit treated with nitric acid was tested for that metal.

RESULTS.

| Gold. Gram. | Copper. Gram. | Potassium cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Gold found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1665 | 1 | 2 | 250 | $N.D._{.175}$=0.07 A. | 1.7 | 65° | $2\frac{1}{2}$ | 0.1667 |
| 0.1627 | 1 | 2 | 250 | $N.D._{.175}$=0.05–0.08 A. | 1.9 | 65° | 3 | 0.1627 |

*Gold from Nickel.*—The conditions under which this separation is made are similar to those obtained *under* the separations of silver and mercury from nickel. The solution of gold chloride used was equivalent to 0.1610 gram of metallic gold, and nickel nitrate contained one-tenth gram of nickel. They were converted into their double cyanides by the addition of four grams of potassium cyanide. A current of $N.D._{.100} = 0.05$ A and $V = 1.5$ was passed through the solution (125 cc.) at 60° for six hours. The gold on examination contained no nickel.

RESULTS.

| Gold. Gram. | Nickel. Gram. | Cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Gold found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1567 | 0.1 | 4 | 125 | $N.D._{.100}$=0.05 A. | 1.7 | 65° | 7 | 0.1567 |
| 0.1610 | 0.1 | 4 | 125 | $N.D._{.100}$=0.05 A. | 1.5 | 60° | 7 | 0.1603 |

*Gold from Cobalt.*—More difficulty was experienced with the separation of these metals than with the preceding. Four grams of potassium cyanide were added to the solution of gold chloride and cobalt nitrate equivalent to one-tenth gram of cobalt. The current used for the deposition of the gold was $N.D._{.100} = 0.05$ A and $V = 1.7$. The electrolysis was carried out at 60° C. It was found advantageous before the end to add one cc. of a twenty per cent. sodium hydroxide solution, and raise the current to 0.08 A, in order to deposit the last trace of gold. In this way the gold was entirely deposited in seven hours free from cobalt.

RESULTS.

| Gold. Gram. | Cobalt. Gram. | Cyanide. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Dilution. cc. | Time. Hours. | Gold found. Gram. |
|---|---|---|---|---|---|---|---|---|---|
| 0.1610 | 0.1 | 4 | 125 | $N.D._{100}$=0.05–0.08 A. | 1.7 | 60° | 125 | 6¾ | 0.1612 |
| 0.1610 | 0.1 | 4 | 125 | $N.D._{100}$=0.05–0.08 A. | 1.7 | 60° | 125 | 6 | 0.1608 |
| 0.1495 | 0.1 | 4 | 250 | $N.D._{175}$=0.05–0.08 | 1.7–2 | 60° | 250 | 6 | 0.1497 |

*Gold from Zinc.*—These metals were successfully separated according to the following conditions: Four grams of potassium cyanide were added to a solution of gold chloride and zinc sulphate containing one-tenth gram of zinc. The current acting upon the double cyanides was $N.D._{100} = 0.06$ A and $V = 2.66$. The temperature of the solution was 60°. In seven hours the deposition was complete. No zinc was found with the gold.

RESULTS.

| Gold. Gram. | Zinc. Gram. | Cyanide. Grams. | Current. | Voltage. | Dilution. cc. | Temperature. | Time. Hours. | Gold found. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1495 | 0.1 | 4 | $N.D._{100}$=0.06 A. | 2.66 | 125 | 60° | 7 | 0.1490 |
| 0.1608 | 1. | 4 | $N.D._{175}$=0.06 A. | 2.7 | 250 | 65° | 7 | 0.1602 |

*Gold from Platinum.*—To the solution of gold chloride containing 0.1576 gram of gold and platinic chloride equivalent to 0.125 gram of platinum, were added one and five-tenths grams of potassium cyanide. The volume of the solution was 250 cc. A current of $N.D._{175} = 0.01$ A and $V = 2.7$ was used. The temperature was 70° C. In three hours the gold was entirely precipitated. No platinum was deposited with the gold. The deposit weighed 0.1479 gram.

*Mercury from an Alkaline Sulphide Solution.*—In 1891 Smith made the statement that mercury obtained as mercuric sulphide, during analysis may be accurately estimated electrolytically. The sulphide was dissolved in sodium sulphide of sp. gr. 1.19, and electrolyzed with a current generating one cc. of oxyhydrogen gas per minute, acting during the night. The mercury was always compact and gray in color.

In working out conditions for the determination of mercury by this method, twenty-five cc. of sodium sulphide were added to a solution of mercuric chloride containing 0.1403 gram of mercury. This solution, diluted to 125 cc., was electrolyzed at 70° C. by a current of $N.D._{100} = 0.11$ A and $V = 2.5$. In five hours the mercury was entirely deposited. It was light gray in

color. Slightly warm water was used in washing the deposit.

RESULTS.

| Mercury. Gram. | Sodium sulphide, sp. gr. 1.19. cc. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Mercury found. Gram. | Error. Gram. |
|---|---|---|---|---|---|---|---|---|
| 0.1403 | 25 | 100 | $N.D._{100}$=0.11 A. | 2.5 | 70° | 5 | 0.1400 | 0.0003 |
| 0.1403 | 25 | 100 | $N.D._{100}$=0.12 A. | 2.7 | 70° | 5 | 0.1404 | 0.0001 |

**COPPER.**

"Moore advises dissolving the recently precipitated copper sulphide obtained during the ordinary course of analysis in potassium cyanide, and after the addition of an excess of ammonium carbonate, electrolyze the warm (70°) solution."[1] According to this suggestion the following conditions for the determination of copper were found to give good results: The copper sulphate solution used contained 0.1270 gram of metallic copper. This was precipitated as sulphide, which was dissolved in two grams of potassium cyanide and ammonium carbonate added. The solution, diluted to 125 cc., was heated to 70° C. and electrolyzed with a current of $N.D._{100} = 0.02–0.07$ A and $V = 4$. In three hours the copper was completely deposited. The copper was found to weigh 0.1269 gram, that is 0.0001 gram less than the theoretical amount.

*Copper from Nitric Acid Solution.*—Copper has also been successfully determined electrolytically in a nitric acid solution.[2] A solution containing ten cc. of concentrated nitric acid was diluted to 100 cc. and electrolyzed. The current used was $N.D._{100} = 0.03$ A and $V = 1.7$. At the ordinary temperature in sixteen hours 0.1396 gram of copper was precipitated. The solution treated with ammonium hydroxide showed that the copper had been entirely deposited. With a temperature of 65° and a current of $N.D._{100} = 0.09$ A and $V = 1.9$ in five hours 0.1397 gram of copper was found, and another determination under identical conditions gave the theoretical amount of copper present.

RESULTS.

| Copper. Gram. | Nitric acid. cc. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Copper found. Gram. |
|---|---|---|---|---|---|---|---|
| 0.1398 | 10 | 100 | $N.D._{100}$=0.03 A. | 1.7 | cold | 16 | 0.1396 |
| 0.1398 | 10 | 100 | $N.D._{100}$=0.09 A. | 1.9 | 70° | 16 | 0.1397 |
| 0.1398 | 10 | 100 | $N.D._{100}$=0.09 | 1.9 | 65° | 16 | 0.1398 |

[1] Smith's Electro-Chemical Analysis, p. 61.

[2] *Am. Chem. J.*, 12, 329.

*Cadmium from Sulphuric Acid Solution.*—Smith[1] describes the quantitative deposition of cadmium from its sulphuric acid solution. Cadmium oxide was dissolved in sulphuric acid. The solution contained two cc. of free sulphuric acid of sp. gr. 1.095. The volume of the solution was twenty-five cc. In two hours the cadmium was completely precipitated. The amount of cadmium present was 0.0931 gram. The following conditions were found to give good results by this method. A solution of cadmium sulphate containing 0.1599 gram of metal after adding three cc. of sulphuric acid, sp. gr. 1.09, and diluting to 125 cc., was electrolyzed with a current of $N.D._{100} = 0.078$ A and $V = 2.61$. The temperature during the electrolysis was 65°. In five hours the deposition of cadmium was complete. The metal weighed 0.1604 gram.

## BISMUTH.

Smith and Thomas[2] deposited bismuth from a citrate solution which contained an excess of sodium citrate. Bismuth hydroxide was dissolved in citric acid and sodium hydroxide added to alkaline reaction. Smith[3] also states that bismuth may be precipitated from an alkaline citrate solution, and a solution containing free citric acid. The conditions under which the deposition took place are not recorded. The following experiments were accordingly made in order to obtain the proper working conditions.

*Bismuth from an Ammonium Citrate Solution.*—A bismuth nitrate solution was made, adding sufficient nitric acid to the salt to prevent the formation of a basic nitrate on the addition of water. To a solution of this salt containing 0.1882 gram of metallic bismuth were added three grams of citric acid and the solution made ammoniacal. It was diluted to 125 cc. The temperature was raised to 70° C. A current of $N.D._{100} = 0.02$ A and $V = 1.8$ was allowed to act for three hours. At the expiration of this time the current was increased to $N.D._{100} = 0.04$ A and $V = 2.3$. Finally, in order to deposit the last traces of the metal held in solution the current was made $N.D._{100} = 0.09$ A. The deposit of bismuth obtained in this way was light

[1] *Am. Chem. J.*, 2, 42.
[2] *Ibid.*, 5, 114.
[3] Smith's Electro-Chemical Analysis, p. 69.

gray in color, very compact and adherent. In one case the current acted all night and the deposit was darker in color, but adherent and easily washed. There was a noticeable amount of the bismuth peroxide deposited. The anode was weighed therefore before and after the electrolysis, and from the weight of the bismuth peroxide found, the amount of the bismuth deposited in this way, calculated and added to the weight of that precipitated upon the cathode.

RESULTS.

| Bismuth. Gram. | Citric acid. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Amount found. Gram. |
|---|---|---|---|---|---|---|---|
| 0.1882 | 3 | 125 | $N.D._{.100}=0.02$ (for 3 hours). | 1.8 | 70° all night | 16 | 0.1881 |
| | | | $N.D._{.100}=0.04$ A. | 2.3 | in cold. | | |
| | | | $N.D._{.100}=0.06$ A. | | | | |
| 0.1882 | 3 | 125 | $N.D._{.100}=0.02$ A (for 3 hours). | 1.6 | 70° | $6\frac{3}{4}$ | 0.1880 |
| | | | $N.D._{.100}=0.04$ A. | 2 | | | |
| | | | $N.D._{.100}=0.09$ A. | 3 | | | |
| 0.1822 | 3 | 125 | $N.D._{.100}=0.03$ A. | 2 | 65° | 6 | 0.1819 |
| | | | $N.D._{.100}=0.042$ A. | 2.58 | | | |
| | | | $N.D._{.100}=0.09$ A. | 3 | | | |
| 0.1822 | 3 | 125 | $N.D._{.100}=0.03$ A. | 2 | 65° | 6 | 0.1820 |
| | | | $N.D._{.100}=0.042$ A. | 2.6 | | | |
| | | | $N.D._{.100}=0.09$ A. | 3 | | | |

*Bismuth from a Potassium Citrate Solution.*—The solution of bismuth nitrate used contained 0.1777 gram. To this were added seven grams of citric acid, followed by an excess of potassium hydroxide. The solution was diluted to 125 cc. The temperature was 70°. The current for this solution was also low at the beginning and was gradually increased to 0.09 A. The deposit of bismuth peroxide on the anode was treated as indicated in the preceding method. The bismuth was in all cases a gray, compact, adherent deposit.

RESULTS.

| Bismuth. Gram. | Citric acid. Grams. | Dilution. cc. | Current. | Volt. age. | Temperature. | Time. Hours. | Amount found. Gram. |
|---|---|---|---|---|---|---|---|
| 0.1767 | 7 | 125 | $N.D._{.100}=0.02$ A.<br>$N.D._{.100}=0.038$ A. | 2.16<br>2.18 | 65° | 5 | 0.17648 |
| 0.1777 | 7 | 125 | $N.D._{.100}=0.02$ A.<br>$N.D._{.100}=0.05$ A. | 2.5<br>3. | 70° | 5 | 0.1781 |
| 0.1777 | 7 | 125 | $N.D._{.100}=0.03$ A.<br>$N.D._{.100}=0.05$ A. | 2.1<br>2.5 | 65° | $5\frac{1}{2}$ | 0.1774 |

*Bismuth from a Citric Acid Solution.*—Seven grams of citric acid were added to a solution of bismuth nitrate containing 0.1767 gram of bismuth. The solution at 70° was electrolyzed with a current $N.D._{100} = 0.02$ A and $V = 1.8$. Subsequently it was increased to $N.D._{100} = 0.07$ A and $V = 2.6$.

RESULTS.

| Bismuth. Gram. | Citric acid. Grams. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Amount found. Gram. |
|---|---|---|---|---|---|---|---|
| 0.1767 | 7 | 125 | $N.D._{100}$=0.02 A. | 1.8 | 65° | 5 | 0.17648 |
| 0.1767 | 5 | 125 | $N.D._{100}$=0.38 A. | 2.6 | | | |
| | | | $N.D._{100}$=0.02 A. | 1.8 | | | |
| | | | $N.D._{100}$=0.05 A. | 2.66 | 70° | 5 | 0.1761 |

*Mercury from Nitric Acid Solution.*—The fact that mercury could be determined satisfactorily from a nitric acid solution appears in the *Berichte*.[1] Mercuric nitrate was electrolyzed by Smith and Knerr.[2] There was one-half to one cc. of free nitric acid present. Bright, shining deposits of 0.0911 gram were obtained in thirty minutes. The current used for the purpose, liberated four cc. of oxyhydrogen gas per minute.

In the following work three cc. of concentrated nitric acid were added to a solution of mercuric chloride containing 0.1403 gram of metallic mercury. The solution (125 cc.) was electrolyzed with a current $N.D._{100} = 0.06$ A and $V = 2$ for four hours. The temperature was 70° C. The solution in the dish was siphoned off before the interruption of the current.

RESULTS.

| Mercury. Gram. | Nitric acid. cc. | Dilution. cc. | Current. | Voltage. | Temperature. | Time. Hours. | Amount. found. Gram. |
|---|---|---|---|---|---|---|---|
| 0.1403 | 3 | 125 | $N.D._{100}$=0.06 A. | 2 | 70° | 4½ | 0.1404 |
| 0.1403 | 3 | 125 | $N.D._{100}$=0.07 A. | 1.91 | 70° | 4 | 0.1406 |

*Mercury from Sulphuric Acid Solution.*—It has been known for a considerable time that mercury could be deposited from a solution feebly acidulated with sulphuric acid. The current which was used, generated five to six cc. of oxyhydrogen gas per minute. In repeating this method for the precipitation of mercury one cc. of sulphuric acid was added to a solution of mercuric chloride. A current of $N.D._{100} = 0.4$–$0.6$ A and $V = 3.5$ effected the deposition. The temperature during the operation

1 *Ber. d. chem. Ges.*, 19, 329.

2 *Am. Chem. J.*, 8, 206.

was 65° C. The mercury was entirely deposited in one hour. It had a brilliant metallic appearance. It was washed with cold water. The mercury present in the solution was 0.1403 gram. The deposit weighed 0.1402 gram.

*Iron from a Citrate Solution.*—In 1888 Smith reported the deposition of iron from a sodium citrate solution containing free citric acid. The solution used was ferric ammonium sulphate, and the current acting upon the solution gave six cc. of oxyhydrogen gas per minute.

The method was repeated, using a solution of the alum containing 0.0378 gram of metallic iron, ten cc. of sodium citrate, equivalent to 1.18 grams and three cc. of citric acid equivalent to 0.059 gram, and the solution diluted to 125 cc. With a current of $N.D._{100} = 0.58$ A and $V = 5.7$ in seven hours the deposition was complete. Another determination gave 0.0375 gram of iron, and a third gave 0.0379 gram. By titration with potassium permanganate the deposit was found to contain 0.03789 gram of iron. The carbon, therefore, in this deposit was 0.079 per cent.

Similar experiments were conducted, using 0.1035 gram of iron. The current used was $N.D._{175} = 0.8$ A and $V = 9$. The temperature was 60° during the electrolysis. The solution was 250 cc. The deposit weighed 0.1046 gram. By titration of the iron 1.06 per cent. of carbon was found. With identical conditions, using 0.1280 gram of iron 0.94 per cent. of carbon was found deposited in the metal.

RESULTS.

| Iron. Gram. | Citrate. Grams. | Citric acid. Gram. | Current. | Voltage. | Temperature. | Time. Hours. | Found. Gram. | Carbon. Per cent. |
|---|---|---|---|---|---|---|---|---|
| 0.0378 | 10 cc. = 1.18 | 3 cc. = 0.059 | $N.D._{100} = 0.58$ A. | 5.7 | 35° | 7 | 0.0379 | 0.079 |
| 0.0378 | 10 cc. = 1.18 | 3 cc. = 0.059 | $N.D._{175} = 8$–1.3 | 9–11 | 70° | 4 | 0.0383 | 1.1 |
| 0.1035 | 10 cc. = 1.18 | 3 cc. = 0.059 | $N.D._{175} = 8$ | 9–11 | 50° | 4½ | 0.1046 | 1.06 |
| 0.1277 | 10 cc. = 1.18 | 5 cc. | $N.D._{100} = 0.4$-1 A. | 7–11 | 50° | 4½ | 0.1278 | 0.00 |
| 0.1277 | 10 cc. = 1.18 | 5 cc. | $N.D._{100} = 0.8$ A. | 7–8 | 50° | 4½ | 0.1280 | 0.94 |

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 44.]

# ACTION OF HYDROCHLORIC ACID GAS UPON SULPHATES, SELENATES, TELLURATES, AND PHOSPHATES.

BY RAYMOND W. TUNNELL AND EDGAR F. SMITH.

Received July 21, 1899.

EXPERIMENTS have been made at various times in this laboratory upon the action of the gaseous haloid acids on metallic oxides and sulphides. Frequently new methods of separation have resulted. These have proved very satisfactory in every respect, from the standpoint of the analyst.

In the following paragraphs we give additional data collected from the same field, and trust that they may not be devoid of interest to the reader.

Knowing that selenic and telluric acids could be expelled from their salts by hydrochloric acid gas we endeavored to ascertain whether, if a sulphate were mixed with one or both of the preceding salts, it would be possible to drive out the selenic or telluric acid and leave the sulphate intact. Accordingly a perfectly dry mixture of a sulphate and a selenate was exposed to the action of well-dried hydrochloric acid gas. The selenic acid was not only expelled but also varying amounts of sulphuric acid were driven out. Thus, two trials were made with definite amounts of the salts. The results were these:

| Potassium sulphate taken. Gram. | Potassium selenate taken. Gram. | Sulphur remaining in the salt acted upon. Per cent. |
|---|---|---|
| 0.4323 | 0.4567 | 33.59 |
| 0.3338 | 0.1583 | 33.51 |

In brief, about sixty-five per cent. of the sulphur originally contained in the potassium sulphate was expelled in the presence of the selenate. When a tellurate was mixed with the sulphate and the two subjected to the action of hydrochloric acid gas, not only was the tellurium driven out from its combination but the sulphur also in amounts, which varied with the working conditions. The original idea, therefore, of effecting a separation was abandoned.

We next exposed pure, dry potassium sulphate to the influence

of the haloid acid. A weighed amount of the salt was introduced into a porcelain boat, placed in a combustion tube of hard glass, through which the gas was conducted in the cold. It was very soon observed that the salt had increased very considerably in weight (as much as twelve per cent). After a time the boat was removed and the residue in it analyzed. Thus, 1.0896 grams of potassium sulphate after exposure for three and one-half hours to the gas, in the cold, weighed 1.1162 grams—an increase of 0.0266 gram. The salt was dissolved in water and the hydrochloric acid in it determined. It equaled 0.0268 gram, or a difference of 0.0002 gram from the observed increase in weight. This product (an addition product evidently) maintained its composition when exposed to 130° in a drying oven. It did not lose in weight on standing over soda-lime, in a vacuum desiccator, for fifteen hours.

When dry potassium sulphate was heated in hydrochloric acid gas from 200° to a dull red heat, an examination of the water in the receiving vessel showed the presence of sulphuric acid, while the substance remaining in the boat after this treatment weighed more than the original substance. It gave an acid reaction to litmus and decolorized a red phenolphthalein solution. As much as nineteen per cent. of the sulphuric acid in the salt was expelled in this way. The quantity of acid driven out was greater in the presence of a selenate or tellurate, equaling in several instances seventy-five per cent.

This deportment of sulphuric acid confirms an early observation of Heusgen,[1] who found that "Kalium sulfat wird weder in der Kälte noch bei gewöhnlicher Temperatur von Salzsäure angegriffen ..... bei 360° liess sich in dem vorgelegten Wasser schon eine wägbare Menge Schwefelsäure nachweisen, bei dunkler Rothgluth erfolgt jedoch die Zersetzung *fast* quantitativ in Chlormetall und freie Schwefelsäure." The gas evidently attacks the salt in the cold. This is proved by the formation of the addition product. We never observed a complete elimination of the sulphuric acid. It was not, indeed '*fast quantitative.*' And, Prescott,[2] trying the action of aqueous hydrochloric acid upon metallic salts, observed that upon evaporating a gram of sodium sulphate with 4.035 grams of

[1] *Ber. d. chem. Ges.*, (1876), 1671.

[2] *Chem. News*, **36**, 178.

aqueous hydrochloric acid, containing 1.251 grams of hydrochloric acid, he obtained only 0.070 gram of sodium chloride, and 0.807 gram of undecomposed sulphate remained.

The question as to how the sulphuric acid is expelled from its salt is worth consideration. The thought first suggested was that the addition compound, $K_2SO_4 + HCl$, is produced when the gas acts upon the salt, and this upon the application of heat decomposes, forming potassium chloride and acid potassium sulphate, the latter being changed by the same heat into $2KHSO_4 = K_2SO_4 + H_2O + SO_3$. If this were true then the addition compound, which in theory was formed at first, when heated alone in dry air should give up its sulphuric acid in part at least and it should be found in the water of the receiver. Several trials were made. Sulphuric acid was not found in the receiver, but instead about eighty-six per cent. of the hydrochloric acid originally present with the potassium sulphate was discovered to be there. After numerous experiments of various sorts we concluded that this remarkable expulsion of sulphuric acid from one of its stable salts is to be attributed to mass action. This is emphasized by its more complete expulsion when a selenate or a tellurate is present.

It is a well-established fact that phosphoric acid is not expelled by the gaseous haloid acids from its salts.

A mixture of dry sodium tellurate and dry sodium pyrophosphate was exposed to the action of hydrochloric acid gas. Care was taken that the temperature did not become so intense as to melt the mass in the boat. When this occurs the telluric acid is apparently reduced very rapidly. In the analysis, which will be introduced, the tellurium was merely expelled. No attempt was made to estimate its amount. The residual phosphate, after solution in water, was invariably examined for tellurium but it was not detected. The phosphoric acid was determined in the usual manner.

ANALYSES.

| | Phosphorus present in the $Na_2P_2O_7$. Gram. | Amount of sodium tellurate taken. Gram. | Phosphorus found as $Mg_2P_2O_7$. Gram. |
|---|---|---|---|
| 1 | 0.1030 | 0.1247 | 0.1026 |
| 2 | 0.1197 | 0.1632 | 0.1199 |
| 3 | 0.1096 | 0.0832 | 0.1094 |

Sodium selenate was next mixed with sodium pyrophosphate. Much less time was required for the volatilization of the selenic acid than for that of the telluric acid. The temperature was gradually raised to 450°C. It was not allowed, nor was it necessary, to go beyond this point.

ANALYSES.

| | Phosphorus present in the $Na_2P_2O_7$ used. Gram. | Sodium selenate. Gram. | Phosphorus found as $Mg_2P_2O_7$. Gram. |
|---|---|---|---|
| 1 | 0.0728 | 0.1763 | 0.0729 |
| 2 | 0.1057 | 0.2017 | 0.1054 |
| 3 | 0.1198 | 0.1416 | 0.1199 |

The preceding results with phosphates and tellurates and those with selenates and phosphates leave no doubt as to the complete separation of their respective acids, in the manner indicated. The method is free from all disturbing factors and may be executed without difficulty.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 45.]

## THE PRECIPITATION OF COPPER BY ZINC.

BY JOHN C. SHENGLE AND EDGAR F. SMITH.

Received August 2, 1899.

AT various times during the past year attempts have been made in this laboratory to make a direct comparison between silver and cadmium, with the hope that in this way the atomic mass of the latter metal might be definitely established. The most carefully purified metallic cadmium in weighed amounts was allowed to act upon various soluble salts of silver. The precipitation of the latter metal was rapid and complete. The results while very fair in a quantitative respect could not be used for the purpose designed. The precipitated silver contained cadmium. It was not undissolved portions of the latter but metal originating from the salt which was acted upon, which salt became in some way encased in the silver so that the most painstaking efforts failed to eliminate it. Nor did it seem to make any difference as to which silver salt was acted upon. Cadmium, in small amounts it is true, but nevertheless, cadmium was invariably discovered in the beautiful deposits of silver.

When copper salts were substituted for silver salts, the cadmium threw out the copper quickly and in calculated amounts, but it also was contaminated with varying quantities of cadmium, so that the scheme originally planned for the determination of the atomic mass of cadmium was abandoned.

This negative experience suggested the idea of testing the copper precipitated by metallic zinc. This being a method recommended for the quantitative estimation of copper we concluded to ascertain if possible whether it carried or retained any zinc. Pure copper sulphate was prepared, and metallic zinc was also obtained pure by the distillation method of Morse and Burton.[1]

The determinations were conducted in the usual manner, but instead of weighing the precipitated copper it was dissolved in nitric acid and estimated by means of the electric current. The liquor poured off from this deposit was examined for the zinc.

ANALYSES.

1. Twenty cc. of a copper salt solution, containing 0.1739 gram of copper, was precipitated by metallic zinc. The deposit of copper was filtered, thoroughly washed, dried, and dissolved in acid, and its solution electrolyzed, the filtrate from the copper deposit being used for the determination of any contaminating zinc:

| | Copper present. Gram. | Copper found. Gram. | Zinc found. Gram. |
|---|---|---|---|
| I | 0.1739 | 0.1742 | 0.0067 |

In the second and third determinations the results were:

| | Copper present. Gram. | Copper found. Gram. | Zinc found. Gram. |
|---|---|---|---|
| II | 0.1739 | 0.1741 | 0.0027 |
| III | 0.2609 | 0.2612 | 0.0033 |

Twenty-two precipitations were made with varying conditions. Zinc was found in all of the precipitated copper. As a rule this method gives fair results, but it is notwithstanding interesting to know that the good results must be due largely to a balancing of errors.

[1] *Am. Chem. J.*, 10, 148, (1888).

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, NO. 46.]

# THE PERSULPHATES OF RUBIDIUM, CESIUM, AND THALLIUM.

BY ARNOTT R. FOSTER AND EDGAR F. SMITH.

Received August 2, 1899.

SINCE Hugh Marshall prepared a number of persulphates these salts have attracted considerable attention both from a theoretical and practical standpoint. As the potassium and ammonium salts are generally those which are made and with which experiments are conducted we concluded to attempt the production of the persulphates of rubidium and cesium. We employed a "divided cell," using for the purpose that one recommended by Nernst which is so convenient that it should become a valuable adjunct in class experimentation.

## RUBIDIUM PERSULPHATE.

To obtain this salt a solution consisting of two-thirds part sulphuric acid (1.35 sp. gr.) and one-third part of a saturated rubidium sulphate solution was electrolyzed, the cell being surrounded by a freezing-mixture of sodium chloride and ice.

Anode surface 1.575 sq. cm..... ..... 0.45 A.
Voltage..... 8

A white precipitate began to separate at the anode after twenty minutes. The deposition at first was very slow, but later it became more rapid. The deposit was freed by filtration from the adherent liquid by washing it with cold water. Its aqueous solution oxidized a ferrous salt and liberated iodine from potassium iodide. The salt crystallized from water in acicular, vitreous forms.

### *Analysis.*

The available oxygen was determined with ferrous ammonium sulphate and potassium permanganate. The oxidation proceeded slowly so that heat was applied to the solution of the persulphate and iron ammonium sulphate in an atmosphere of carbon dioxide. The oxygen liberated by ignition from a given quantity of the salt in an atmosphere of carbon dioxide was collected over caustic potash and measured.

I. 0.3381 gram of the persulphate on ignition gave 0.2484 gram of rubidium sulphate or 73.47 per cent., instead of 73.51 per cent., required by theory.

II. 0.2608 gram of the persulphate, acting upon ferrous ammonium sulphate (2.3633 grams), showed the presence of 0.0129774 gram of oxygen, equivalent to 4.69 per cent., instead of 4.41 per cent. (calculated).

III. A second titration of the persulphate was made with 0.2608 gram of the salt and 2.7190 grams of ferrous ammonium sulphate, when 0.11884 gram of oxygen was found, equivalent to 4.55 per cent., instead of 4.41 per cent.

IV. Oxygen by volume. 0.3254 gram of the persulphate gave 11.7 cc. of oxygen at 27° and 773 mm. pressure, or 0.01486784 gram equivalent to 4.56 per cent., instead of 4.41 per cent.

These results, therefore, conclusively demonstrate that rubidium persulphate, $K_2Rb_2O_8$ or $KRbO_4$, really does exist.

V. Meyer's method was used in determining the solubility of this salt. 100 parts of water dissolved (1) 3.32 parts and (2) 3.49 parts of the salt at 22.5° C.

## CESIUM PERSULPHATE.

It was formed by electrolyzing a chilled mixture of two-thirds part sulphuric acid (sp. gr. 1.35), and one-third part of a saturated cesium sulphate solution in the same manner as with rubidium sulphate.

| | |
|---|---|
| Anode surface 1.57 sq. cm | 0.32 ampere. |
| Voltage | 6 |

A white deposit began to form at the anode in fifteen minutes. It separated even more rapidly than in the case of the rubidium persulphate. It was filtered out, washed thoroughly and analyzed. Its aqueous solution showed oxidizing properties, liberating iodine from potassium iodide and converting ferrous into ferric salts. The persulphate also crystallizes in colorless needles. Its analysis proved less satisfactory than that of the corresponding rubidium salt. It was difficult to obtain constant weight by ignition. The volume of oxygen was generally too high, although the results obtained by titration were entirely satisfactory.

*Analysis.*

I. 0.4348 gram of the salt and 2.0797 grams of ferrous ammonium sulphate, showed the presence of 0.0143 gram of oxygen, equivalent to 3.31 per cent., instead of 3.50 per cent.

II. 0.2612 gram of the persulphate and 2.1132 grams of ferrous ammonium sulphate showed 0.008439 gram of oxygen, equal to 3.59 per cent., instead of 3.50 per cent., by theory.

Upon determining the solubility of the persulphate by V. Meyer's method, it was found that 100 parts of water dissolved 8.71 parts of the salt at 23° C.; again, 100 parts dissolved 8.98 parts of the persulphate at the same temperature.

THALLIUM PERSULPHATE.

As thallium in some respects resembles the alkali metals, it occurred to us that perhaps it might also yield a persulphate. Accordingly, a saturated solution of its sulphate, treated with sulphuric acid (sp. gr. 1.70), as in the preceding examples, was chilled and electrolyzed.

Anode surface 1.57 sq. cm..... 0.45 A.
Voltage..... ..... 14

At the expiration of an hour a white precipitate began to separate at the anode. It proved to be very soluble in water, and difficulty was experienced in getting it pure. In fact it decomposed so rapidly in the air that the analysis of it was abandoned. Its aqueous solution rapidly oxidized ferrous salts and set iodine free from potassium iodide. More than this we cannot offer for this salt which is undoubtedly produced in the oxidation of thallous sulphate.

## THE CHROMIC ACID TEST FOR COCAINE.

By George L. Schaefer.

Received July 7, 1899.

SINCE the publication of my proposed new test for cocaine, several articles have appeared in criticism thereof, which call for some reply.

P. W. Squire[1] states that the test "produces a turbidity in solutions of the best commercial samples of cocaine hydrochlorate." Further than this he does not go, but in a note appended

[1] "The New Test for Cocaine," *Chemist and Druggist*, April 22.

to his communication, the editor states that the "value of the chromate test is questionable." A. J. Crownley,[1] objects on the ground that the test is too delicate and that only a "synthetic" cocaine would stand it. The most satisfactory reply to these critics is the statement that the finest commercial brands of cocaine hydrochloride satisfactorily answer the chromic acid test.

E. Merck,[2] in criticizing the test states that the strength of the hydrochloric acid will affect the results obtained. In applying the test he found that a solution of cocaine to which he had added five cc. of ten per cent. hydrochloric acid, yielded negative results, and that upon increasing the amount of acid by using five cc. twelve and one-half per cent. hydrochloric acid, a turbidity was produced, thus in the first case showing the cocaine to be pure, and in the second case indicating impurities. This is in accord with my own observations, and the difference in the results is due to the fact that the sample of cocaine employed contained only very minute traces of amorphous alkaloids, the chromates of these latter bodies being far less soluble in the solution containing the higher percentage of hydrochloric acid. The turbidity will therefore be produced more rapidly and more distinctly than in the solution containing the weaker acid. An acid of ten per cent. strength was decided upon, as it is sufficient to indicate such very small traces of amorphous impurities, that only the very best brands of cocaine in the market will stand this test, and it, together with the permanganate test, guarantees a purity of product which cannot be obtained when McLagan's test is taken as the standard. If the reaction is carried out with a stronger acid, it is necessary to do so side by side with a specimen of chemically pure cocaine as at a low temperature cocaine chromate causes a turbidity in the more acid solution.

Merck further claims that the results are influenced by the age of the chromic acid solution. My own experience has failed to prove that such is the case. In a recent series of experiments with a number of samples of cocaine, using the same solution of chromic acid for fourteen consecutive days, and always applying the test side by side with a freshly prepared chromic acid solu-

[1] "Note on a New Test for Cocaine," *Pharmaceutical Journal*, April 15.
[2] "Cocaine Tests," *Pharm. Zlg.*, No. 42.

tion, at no time was there noticed any difference in the results obtained.

In applying the test it is important that the temperature of the cocaine solution be maintained at 15° C., the chromates of both pure cocaine and the amorphous alkaloids being influenced by rise and fall of temperature, heat increasing and cold diminishing their solubility. The test produces no turbidity when the acid is added to a solution of a pure specimen of cocaine, the temperature being 15° C. If, however, the solution be subjected to a considerably lower temperature, it becomes turbid, and if it be preserved at this reduced temperature for several hours, a crystalline deposit will be found, consisting of long needle-shaped crystals of cocaine chromate. A solution of impure cocaine rendered turbid by the reagent at 15° C., and exposed to a lower temperature remains turbid for several hours, then slowly deposits a yellowish-brown amorphous sediment. These reactions are characteristic and serve to distinguish between cocaine and the amorphous alkaloids, especially isatropyl-cocaine. If a stronger acid is used the alkaloids will separate out quicker.

In order to show the superiority of the chromate test over McLagan's test, I prepared a series of specimens of cocaine of different degrees of purity. These, as well as the various brands of cocaine in the market, I subjected to McLagan's and the chromate test. As a result, I found specimens which gave negative results with McLagan's test, to be impure by the chromate test, and those specimens which reacted with McLagan's test yielded a decided turbidity upon the addition of even less than five cc. of the ten per cent. hydrochloric acid.

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## NOTES.

*On the Reichert Figure of Butter.*—During the last few years I have had occasion to examine a great many samples of butter, intended for exportation to Venezuela and other South American ports. As many of these samples were of very low grade, it occurred to me that a compilation of the Reichert figures obtained might be of interest to those engaged in this line of work, and I therefore take pleasure in submitting to the society the results of some 317 analyses, taken at random from my

laboratory books, and representing butter exported by five firms during the years 1897, 1898, and 1899.

The figures obtained are as follows:

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 15.2 | 14.7 | 13.1 | 15.3 | 16.6 | 12.5 | 15.6 | 12.5 |
| 15.2 | 13.9 | 13.6 | 14.7 | 15.8 | 13.6 | 16.0 | 12.2 |
| 13.8 | 14.0 | 13.4 | 14.9 | 17.0 | 15.1 | 15.0 | 12.3 |
| 14.8 | 13.3 | 17.0 | 14.3 | 16.1 | 16.6 | 16.2 | 13.4 |
| 13.0 | 13.9 | 17.8 | 13.6 | 17.0 | 15.2 | 16.6 | 13.6 |
| 13.8 | 14.3 | 13.7 | 13.7 | 17.0 | 14.6 | 14.8 | 13.7 |
| 13.8 | 14.2 | 13.2 | 15.3 | 15.3 | 13.5 | 17.0 | 16.2 |
| 13.7 | 14.3 | 13.2 | 16.3 | 16.1 | 16.2 | 14.6 | 17.5 |
| 14.4 | 13.9 | 15.8 | 15.9 | 13.6 | 13.9 | 14.2 | 15.9 |
| 14.0 | 14.9 | 14.7 | 15.1 | 15.4 | 13.9 | 13.8 | 14.6 |
| 16.6 | 13.1 | 12.6 | 16.4 | 13.6 | 14.7 | 15.3 | 13.9 |
| 14.3 | 15.6 | 16.2 | 14.7 | 15.6 | 15.8 | 16.4 | 15.7 |
| 15.4 | 14.0 | 16.2 | 15.2 | 14.2 | 13.6 | 15.8 | 14.7 |
| 14.0 | 14.2 | 14.2 | 12.0 | 14.3 | 16.7 | 14.0 | 18.2 |
| 14.2 | 12.6 | 12.0 | 13.8 | 14.7 | 16.9 | 14.0 | 15.5 |
| 15.4 | 15.0 | 15.1 | 13.2 | 15.0 | 14.5 | 15.0 | 14.0 |
| 16.5 | 15.2 | 14.5 | 13.2 | 13.9 | 16.0 | 15.1 | 13.0 |
| 13.2 | 15.3 | 12.5 | 16.0 | 14.8 | 16.2 | 15.0 | 14.0 |
| 12.6 | 15.6 | 12.8 | 13.6 | 13.5 | 15.0 | 15.9 | 17.2 |
| 14.4 | 13.8 | 11.2 | 17.2 | 12.4 | 13.8 | 13.0 | 11.7 |
| 14.2 | 14.0 | 12.8 | 15.3 | 14.0 | 14.2 | 12.8 | 15.0 |
| 13.6 | 14.0 | 13.5 | 15.7 | 14.1 | 17.6 | 14.7 | 15.4 |
| 14.7 | 16.2 | 12.7 | 15.5 | 14.0 | 15.8 | 15.6 | 13.8 |
| 14.8 | 15.9 | 13.0 | 16.6 | 16.0 | 13.7 | 14.8 | 16.0 |
| 14.7 | 17.0 | 13.1 | 15.5 | 13.8 | 13.9 | 15.0 | 14.3 |
| 13.4 | 15.5 | 14.6 | 15.5 | 13.6 | 14.9 | 14.8 | 14.9 |
| 14.8 | 14.2 | 15.5 | 13.4 | 15.0 | 15.5 | 15.0 | 13.5 |
| 15.2 | 13.8 | 16.6 | 13.8 | 15.4 | 13.4 | 16.2 | 13.8 |
| 16.6 | 15.2 | 16.0 | 14.2 | 13.6 | 14.8 | 16.6 | 13.5 |
| 14.9 | 13.4 | 16.2 | 15.8 | 12.5 | 14.5 | 16.0 | 16.3 |
| 14.8 | 11.4 | 16.0 | 13.0 | 14.3 | 12.8 | 17.4 | 16.5 |
| 13.8 | 13.4 | 15.7 | 15.0 | 15.1 | 14.2 | 17.7 | 16.2 |
| 16.9 | 13.8 | 14.7 | 14.0 | 14.3 | 15.6 | 15.8 | 15.7 |
| 14.6 | 13.6 | 14.0 | 13.6 | 16.4 | 14.0 | 16.9 | 13.6 |
| 16.2 | 13.5 | 13.5 | 12.8 | 13.4 | 13.3 | 15.4 | 12.8 |
| 16.1 | 13.8 | 14.1 | 14.9 | 15.8 | 14.7 | 14.7 | 14.5 |
| 15.4 | 14.0 | 14.5 | 14.1 | 15.4 | 15.6 | 15.7 | 16.1 |
| 16.6 | 14.5 | 15.0 | 15.6 | 14.1 | 15.6 | 13.6 | |
| 16.2 | 15.1 | 15.5 | 13.0 | 13.0 | 14.1 | 15.0 | |
| 15.6 | 14.7 | 15.3 | 14.6 | 12.8 | 16.4 | 12.0 | |

The average of these 317 tests is 14.7. The highest figure obtained was 18.2, and the lowest figures found were 11.2, 11.4, and 11.7.

The butters which gave these last three figures I at first blush suspected of being adulterated with some foreign fat, but subsequent tests showed this not to be the case. The three butters in question were all samples of winter butter, the one giving the figure 11.2 having been kept so long that it was on the verge of becoming tallowy, while the other two were decidedly rancid.

Although the above were samples of unadulterated butter, I, nevertheless, refused to pass them on the strength of the Reichert figure alone, as they were so far below the standard usually accepted by chemists.

Reichert found true butters to give numbers ranging from 13.55 to 14.55, with an average of 14, and declared any butter giving less than 12 must be adulterated.

Dr. G. C. Caldwell reported to the N. Y. State Board of Health estimations of twenty-seven samples of butter, yielding Reichert figures running from 12.7 to 15.5.

Waller and Martin (Report N. Y. State Dairy Commission, 1886) obtained from twenty-six samples of American butters Reichert figures of 12.2 to 16.3.

Prof. C. B. Cochran, West Chester, Pa., Food Inspector of the Pa. Board of Agriculture, has found the extreme minimum of the Reichert numbers of known genuine butters to be 12.5, and this chemist holds that the proper minimum is 11.5.

From the above it will be seen that there is a divergence of views as to what properly constitutes the lowest allowable Reichert figure for butters of known genuineness, but, from my own experience, I am in favor of placing the limit at 11.5.

I do not consider that it would be prudent to go much below this, so as to cover such extreme cases as I have just mentioned, as in cases of this kind it would not do to rely upon the Reichert number alone, the chemist only consenting to pass upon such products after satisfying himself as to their purity, by submitting them to a thorough examination. JAMES H. STEBBINS, JR.

*Analysis of Zinc for Cadmium and Lead.*—Place fifty grams zinc in a large beaker with 700–800 cc. water and 120 cc. hydrochloric acid (1.20 sp. gr.) and allow to stand over night. The greater portion of zinc is dissolved and removed by decantation. The lead and cadmium are precipitated on residual zinc.

After solution of the lead, cadmium, and residual zinc in dilute

nitric acid, sulphuric acid is added and nitric acid evaporated off. The lead and cadmium sulphates are boiled with water to dissolve cadmium sulphate, and after cooling, lead sulphate is filtered off and determined in the usual manner.

The cadmium in the filtrate is precipitated by hydrogen sulphide and after precipitation, the filter containing the precipitate is placed in a flask and cadmium sulphide dissolved in hydrochloric acid. After driving off the hydrogen sulphide by boiling, fifty cc. of a solution of zinc chloride containing ten grams zinc per liter is added, and cadmium and zinc titrated together with potassium ferrocyanide solution containing 36.76 grams potassium ferrocyanide per liter.

The ferrocyanide solution is standardized by titrating 50 cc. of the zinc solution, the difference between the amount required for the zinc solution and the solution containing cadmium and zinc is the amount required for cadmium precipitation. Each cc. of the ferrocyanide solution should precipitate 0.01 gram cadmium or 0.0085 gram zinc, zinc requiring 4.328 grams potassium ferrocyanide to precipitate one gram zinc.

The titration of small quantities of cadmium without addition of either zinc or more cadmium is inaccurate.

TITRATION OF CADMIUM BY POTASSIUM FERROCYANIDE.

The formula of cadmium ferrocyanide as usually given is $K_2CdFe(CN)_6$, the reaction between cadmium salts and potassium ferrocyanide being thus:

$$CdCl_2 + K_4Fe(CN)_6 = K_2CdFe(CN)_6 + 2KCl.$$

This will require 3.767 gram-molecules of potassium ferrocyanide to precipitate one gram-molecule of cadmium. In practice by titration of a commercially pure cadmium it was found to take 3.676 gram-molecules or a difference of two and one-half per cent.

The titration is as follows: 3.676 grams of potassium ferrocyanide are dissolved in a liter of water and the hot cadmium solution is titrated after addition of ammonium chloride in the same manner as zinc, using uranium acetate as indicator, the end-reaction being distinct. The cadmium ferrocyanide is white, as is zinc ferrocyanide, and as a result, zinc analyses by the ferrocyanide method will be high in proportion as cadmium is present.

P. A. MACKAY.

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## ERRATUM.

In the June number, 1899, page 519, line 18 from bottom, for "fifty grains" read "fifty grams."